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PROCÉDÉ DE PIÉGEAGE DU CO_2 INDUSTRIEL PAR CARBONATATION MINÉRALE DE RÉSIDUS MINIERS SILICATÉS (SERPENTINITE) ET VALORISATION DES SOUS-PRODUITS

Par

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« Deux intellectuels assis vont moins loin qu'une brute qui marche »

Michel Audiard

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AVANT PROPOS

Cette étude présente les travaux réalisés afin d'optimiser et de développer un procédé de séquestration du CO_2 contenu dans un gaz de combustion de composition s'approchant de celui d'une cimenterie par carbonatation minérale en phase aqueuse de résidu miniers. Les résultats obtenus lors de ces travaux de recherche ont entre autre menés au dépôt d'une demande de brevet international, WO2013/131193 A1. Cette thèse est composée de deux sections.

La première section présente la synthèse de cette étude. Celle-ci inclus la revue de littérature, l'énoncé des principaux aspects théoriques rencontrés et les principaux résultats obtenus.

La deuxième section inclus trois articles, dont deux ont été soumis et un en préparation pour une soumission dans des journaux avec comités de lecture ainsi que le résumé de la demande de brevet international :

Reaction mechanism for the aqueous phase mineral carbonation of heat activated serpentine at low temperature and pressure in flue gas conditions, Pasquier, Louis-César; Mercier, Guy; Blais, Jean-Francois ; Cecchi, Emmanuelle; Kentish, Sandra, soumis le 6 décembre 2013 dans la revue Environmental Science & Technology.

Parameters optimisation for direct flue gas CO2 capture and sequestration by aqueous mineral carbonation using activated serpentinite based mining residue, Pasquier, Louis-César; Mercier, Guy; Blais, Jean-Francois ; Cecchi, Emmanuelle; Kentish, Sandra, soumis le 4 décembre 2013 dans la revue Applied Geochemistry.

Economic evaluation and feasibility of a mineral carbonation process using southern Québec mining waste for direct flue gas CO2 sequestration with by product recovery, Pasquier, Louis-César; Mercier, Guy; Blais, Jean-Francois ; Cecchi, Emmanuelle; Kentish, Sandra, en préparation pour soumission dans la revue, Journal of Environmental Management

Carbon dioxide chemical sequestration from industrial emissions by carbonation, WO 2013131193 A1/CA2771111A1, Mercier, Guy; Blais, Jean-Francois ; Cecchi, Emmanuelle; Veetil Sanoopkumar Puthiya; Pasquier, Louis-César; Kentish, Sandra. Demande déposée le 7 mars 2013 (date d'antériorité 7 mars 2012), publiée le 12 septembre 2013.

RÉSUMÉ

Depuis plusieurs années, les techniques de capture et de séquestration du CO_2 ont suscité un grand intérêt de la part de la communauté scientifique. Parmi elles figure la carbonatation minérale, basée sur la réaction entre le CO_2 et un oxyde métallique, principalement de magnésium et de calcium, afin de former des carbonates, stables et inertes. Le sud du Québec, de par son activité minière passée, possède une quantité considérable de résidus riches en Mg (20-40% MgO) de composition proche de la serpentine. Cette étude s'intéresse à l'évaluation du potentiel de séquestration de ces matériaux pour le traitement direct d'un gaz de combustion contenant en moyenne 18% de CO_2, permettant d'éliminer l'étape de capture et de concentration.

La réaction est réalisée en phase aqueuse, à basse température et basse pression dans un réacteur agité. Par ailleurs, afin de compenser les coûts liés aux besoins énergétiques du prétraitement du matériel (broyage et activation thermique), l'accent a été mis sur l'obtention d'un carbonate de magnésium ayant un potentiel de revente. Par conséquent, la précipitation des carbonates est réalisée hors du réacteur, offrant un produit quasi pur. L'optimisation des paramètres opératoires et le développement d'un scenario de recirculations adaptés aux différentes cinétiques de la réaction, a permis d'atteindre un taux d'enlèvement de 65% du CO_2 ainsi que 64% de lixiviation du Mg contenu dans le matériel solide. La précipitation des carbonates est ensuite réalisée à 40°C, à partir de la solution concentrée en CO_2 et Mg dissout obtenue après le contact entre le gaz et les résidus solide.

Le procédé ainsi développé offre un taux de carbonatation du résidu de 0.23 (g CO_2 traité / kg de résidu) soit 64% de la capacité maximale. De plus, la possible revalorisation des sous-produits permet d'offrir bilan économique favorable rendant l'implantation à grande échelle de cette technologie faisable et avantageuse.

Cette thèse est composée de deux parties distinctes. La première propose la synthèse de l'étude, en présentant le contexte à travers une revue de la littérature, ainsi que l'exposé des principaux aspects fondamentaux rencontrés. Les matériels et méthodes sont également décrits, ainsi qu'un résumé des principaux résultats. Ces derniers sont présentés dans la deuxième partie de la thèse à travers trois articles scientifiques et la demande de brevet. La description des mécanismes réactionnels est proposée à travers l'article 1.. Le deuxième article décrit l'optimisation des paramètres opératoires et l'élaboration du schéma de procédé. Ces aspects sont également repris dans la demande de brevet. Enfin le troisième article propose une analyse économique qui permet d'identifier les paramètres ayant le plus d'impacts sur l'application industrielle du procédé développé.

Mots Clefs : Carbonatation minérale, traitement des gaz industriels, séquestration du CO_2, valorisation de résidus miniers

ABSTRACT

For some years, scientific interest on carbon dioxide capture and sequestration technologies has increased. Among the different proposed solutions, mineral carbonation is based on the natural reaction between a metallic oxide contained within a mineral and dissolved CO_2 in order to form, stables and inert carbonates. Southern Quebec intense mining exploitation resulted in massive mining residues accumulations. These tailings which composition is majoritarily serpentinite are rich in Mg (20-40% MgO) and known to naturally sequester CO_2. This study focused on the sequestration potential evaluation of these residues for the direct treatment of a flue gas containing 18% CO_2, avoiding a capture and concentration step.

The reaction is realized at low temperature and low pressure in aqueous conditions in a stirred reactor. In order to counterbalance the costs related with energetic requirements for the solid preconditioning (milling and heat activation), obtaining a pure carbonate with a potential sale value was favored by realizing the precipitation in a further step. Reaction parameters optimization led to achieve 65% CO_2 uptake from the gas and 64% Mg leaching from the solid phase. Carbonates were then precipitated at 40°C from the resulting CO_2 and Mg concentrated solution obtained after contacting the gas and the residues.

The developed carbonation process offers a global carbonation efficiency of 0.23 (gCO_2 treated / kg of residue) giving an overall efficacy of 64%. In addition, the by-products valuation allows offering a positive economical balance, which makes an industrial application of the process feasible and advantageous.

This thesis is composed of two distinct parts. The first one offers the synthesis of this study. The context is described within the literature review. In addition, the major fundamentals aspects encountered are also defined. The materials and methods and the major results are presented with a summary of the major results. The second part of the thesis consists in the results presentation split in three articles and a patent application. The first paper describes the reaction mechanism encountered while the second article focuses on the optimization of the operating parameters and into the process diagram elaboration. These aspects are also presented in the patent application. Finally, the third article focuses on the economics analysis of the developed process, and discusses the parameters sensibility regarding the feasibility of an industrial application.

Keywords : Mineral Carbonation, Industrial flue gas treatment, CO_2 sequestration, mining residues valorization

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ARC: Albany Research Center

BET: Brunauer, Emmett and Teller (modèle d'adsorption pour les gaz)

CCNUC: Convention Cadre des Nations Unies sur les Changements Climatiques

CEPCI: Chemical Engineering Plant Cost Index

CH_4: Méthane

CHNS: Analyseur de Carbone Hydrogène Azote Soufre pour les échantillons solides

Cinorg: Carbone inorganique

CO_2: Dioxyde de Carbone

DRX: Diffraction des Rayons X

EDS: Energy Dispersive Spectrometry

ETH: École Polytechnique Fédérale

GES: Gaz à Effet de Serre

GIEC: Groupement d'Expert Intergouvernemental sur l'Évolution du Climat

HFCs: Hydrofluorocarbures

ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectroscopy

LANL: Los Alamos National Laboratory

MEB: Microscope Électronique à Balayage

$Mg(OH)_2$: Brucite

$Mg_3Si_2O_5(OH)_4$: Serpentine (minéraux) / Serpentinite (roche)

MO: Main d'Oeuvre

Mt eq. CO_2: Mégatonnes d'équivalent CO_2

N_2O: Oxyde Nitreux

PFCs: Hydrocarbures perfluorés

PRP: Potentiel de Réchauffement Planétaire

rpm: Rotations Par Minute

SF_6: Hexafluorure de Soufre

TGA: Thermal Gravimetry Analysis

TOC: Total Organic Carbon

INTRODUCTION

Aujourd'hui, et plus que jamais, les changements climatiques et la réduction des émissions de gaz à effet de serre (GES) sont au cœur des préoccupations environnementales mondiales. Alors que le développement de solutions alternatives à l'utilisation de combustibles fossiles s'impose difficilement, la nécessité de réduire les émissions de GES demeure. Depuis les années 1990, notamment suite aux engagements de Kyoto signés par la quasi-totalité des pays industrialisés, un effort important de recherche est porté sur les techniques de capture et de séquestration du dioxyde de carbone (CO_2).

Cependant, malgré les efforts déployés, aucune technologie n'est encore appliquée à échelle réelle. La séquestration géologique, par exemple, se heurte à des problèmes d'acceptation sociale par manque de réponses quant au devenir du CO_2 une fois injecté dans le sous-sol. Alors que les émissions de CO_2 continuent d'augmenter, le développement de procédés efficaces et rentables reste une priorité. Parmi les différentes méthodologies proposées, la carbonatation minérale s'appuie sur la réaction naturelle entre les cations divalents et le CO_2 dissout dans les eaux de pluie afin de former le carbonate associé. Longtemps vue comme une alternative à la séquestration géologique, cette réaction était utilisée pour faire réagir un gaz concentré en CO_2 après un procédé de capture. Cependant, l'addition des coûts de capture et de purification aux besoins énergétiques nécessaires à l'accélération de la cinétique de la réaction rendent cette application difficilement applicable.

Néanmoins, l'utilisation de la carbonatation comme procédé de traitement direct d'un gaz de combustion industriel reste à être démontrée. De plus, l'abondance de résidus miniers ultramafiques carbonatables à une distance raisonnable de centres industriels rendent une telle application des plus intéressantes pour le Québec, qui lance en 2013 un système de bourse du carbone afin de limiter les émissions de CO_2.

CHAPITRE 1 : SYNTHÈSE

1.1 Revue de littérature

1.1.1 Contexte général

1.1.1.1 Gaz à effet de serre

L'effet de serre est un processus naturel, engendré par des gaz qui bloquent une partie de la chaleur solaire au niveau de l'atmosphère et permet ainsi la vie sur terre (Ministère de l'écologie du développement durable et de l'énergie, 2013). Par définition, un gaz à effet de serre (GES) est un gaz présent dans l'atmosphère, d'origine naturelle ou anthropique, qui absorbe et renvoie les rayons infrarouges en provenance de la surface terrestre, contribuant à l'effet de serre (IPCC, 2006). Cependant, l'augmentation des concentrations de GES comme le CO_2, le méthane (CH_4) ou l'oxyde nitreux (N_2O) liée à l'industrialisation, l'utilisation de combustibles fossiles, la déforestation, ainsi que de certaines méthodes agricoles, provoque un réchauffement global de la terre (IPCC, 2007).

Les principaux GES sont le CO_2, CH_4, N_2O, les hydrofluorocarbures (HFCs), les hydrocarbures perfluorés (PFCs) et l'hexafluorure de soufre (SF_6). Indépendamment des facteurs d'émissions de chaque gaz, les GES sont classés selon leur potentiel de réchauffement planétaire (PRP). Ces valeurs fixées par le groupement d'expert international sur l'évolution du climat (GIEC), comparent le pouvoir de radiation d'un tonne d'un GES à une tonne de CO_2 pendant un temps donné (100 ans). Les valeurs sont présentées au Tableau 1.1.

Tableau 1.1 Principaux GES et leur PRP

Gaz à effet de serre	Potentiel de réchauffement planétaire (PRP)[1]
Dioxyde de carbone (CO_2)	1
Méthane (CH_4)	21
Oxyde nitreux (N_2O)	310
Hydrofluorocarbures (HFCs)	140-11 700
Hydrocarbures perfluorés (PFCs)	6 500-9 200
Hexafluorure de soufre (SF_6)	23 900

[1] Valeurs fournies par IPCC (2007).

1.1.1.2 *Émissions de GES mondiales*

Dans son dernier rapport le groupement intergouvernemental sur l'évolution du climat (GIEC) rapporte que, depuis l'époque pré-industrielle, les émissions mondiales de GES sont imputables à l'activité humaine. Entre 1970 et 2004, les émissions de GES ont augmenté de 70%, avec une hausse de 80% concernant le CO_2, le plus important GES anthropique (IPCC, 2007) (Figure 1.1).

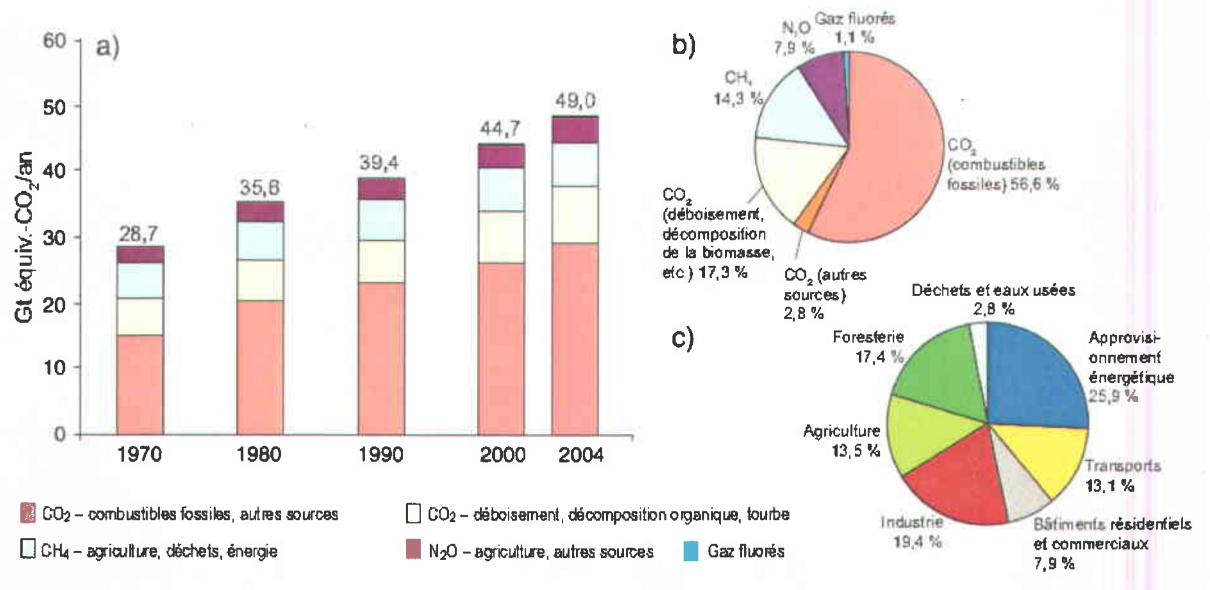

Figure 1.1 **Émissions mondiales de GES anthropiques (IPCC, 2007). a) Émissions annuelles de GES anthropiques dans le monde, 1970–2004. b) Parts respectives des différents GES anthropiques dans les émissions totales de 2004, en équivalent-CO_2. c) Contribution des différents secteurs aux émissions totales de GES anthropiques en 2004, en équivalent-CO_2. (La foresterie inclut le déboisement)**

1.1.1.3 *Émissions canadiennes*

Environnement Canada estime à 702 Mégatonnes d'équivalents CO_2 (Mt eq. CO_2) les émissions canadiennes de GES en 2011, soit 18% de plus par rapport aux émissions de 1990 (Figure 1.2). Lors de la conférence de la Convention Cadre des Nations Unies sur les Changements Climatiques (CCNUC) à Copenhague, les accords de Kyoto qui prévoyaient une réduction des émissions de GES de 5% par rapport au niveau de 1990 en 2012 ont été revus (UNFCC, 2013). La nouvelle cible est une réduction de 17% par rapport aux émissions de 2005 en 2020, soit

612 Mt éq. CO_2. Le secteur de l'énergie est le plus important émetteur de GES au Canada, car il regroupe notamment les émissions liées à la production et à la consommation des combustibles. Dans l'ensemble, ces émissions représentent 73% des émissions totales de 2011 avec 13% de celles-ci issues de la production et de l'extraction du pétrole (Environnement Canada, 2013). Tout comme pour la tendance mondiale, le GES le plus émis au Canada est le CO_2 et représentait 79% des émissions totales.

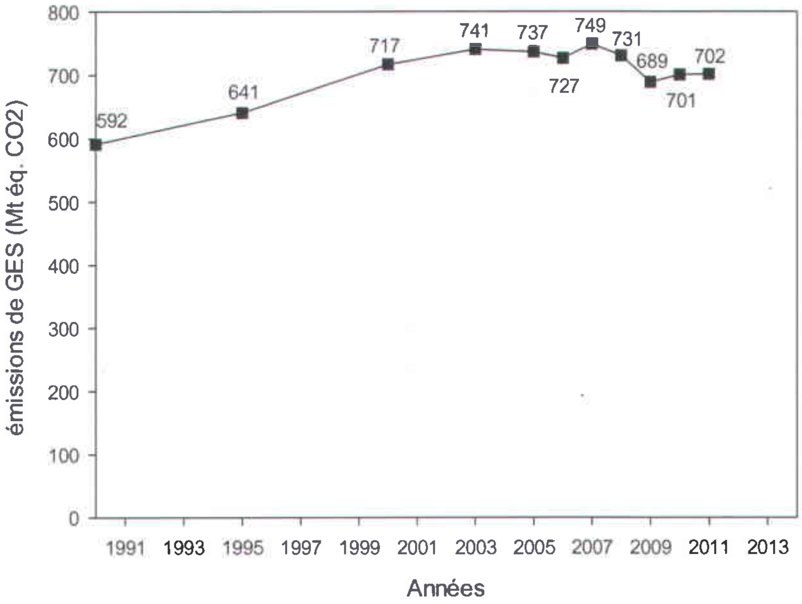

Figure 1.2 **Évolution des émissions totales canadiennes de GES entre 1990 et 2011 (Environnement Canada, 2013)**

1.1.1.4 Émissions au Québec

En 2010, les émissions de la province du Québec se chiffraient à 83.8 Mt eq. CO_2 (MDDEFP 2013) . La répartition par secteur d'activités est ici modifiée. Ainsi, le transport n'est pas inclus au secteur de l'énergie, mais est présenté comme un secteur indépendant. De plus, les émissions du secteur industriel regroupent les émissions liées à la combustion qui sont généralement intégrées au secteur de l'énergie. Ainsi, le secteur d'activités représentant la plus grande part des émissions est le secteur du transport, avec 35.06 Mt eq. CO_2, soit 42.5% des émissions totales

(Figure 1.3). Ce sont également les seules émissions en hausse par rapport aux niveaux de 1990. Ceci peut être en partie attribuable à l'accroissement constant du parc automobile de la province (Institut de la statistique du Québec, 2013).

Mis à part le transport, les émissions des différents secteurs étaient à la baisse en 2010 par rapport à 1990, ce qui explique la diminution de 1.6% des émissions totales (MDDEFP 2013) .

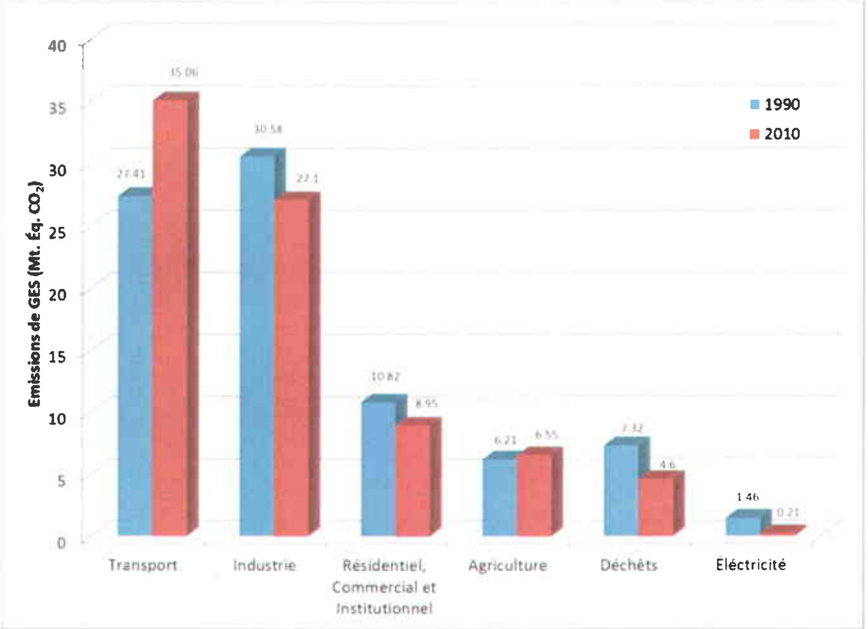

Figure 1.3 **Répartition des émissions de GES par secteur d'activité au Québec en 1990 et 2010 (MDDEFP, 2013)**

1.1.1.4.1 Émissions au sein du secteur industriel (Québec)

Comme abordé précédemment, le secteur industriel représente une importante source de GES au Québec. C'est également le secteur ciblé par cette étude. Cette partie vise à détailler les émissions propres à l'industrie afin de mieux définir le contexte.

Les principaux facteurs d'émissions du secteur industriel sont la combustion des divers combustibles, ainsi que les procédés proprement dit. On retrouve également les émissions liées à l'utilisation de solvants, ainsi que les émissions fugitives, qui sont issues du transport et de la distribution du gaz naturel et des torchères associées au raffinage du pétrole.

D'un point de vue des émissions, le secteur industriel se classe deuxième après le transport, avec 32.9% des émissions totales soit, 27.1 Mt eq. CO_2. La Figure 1.4 présente la répartition des émissions au sein du secteur industriel.

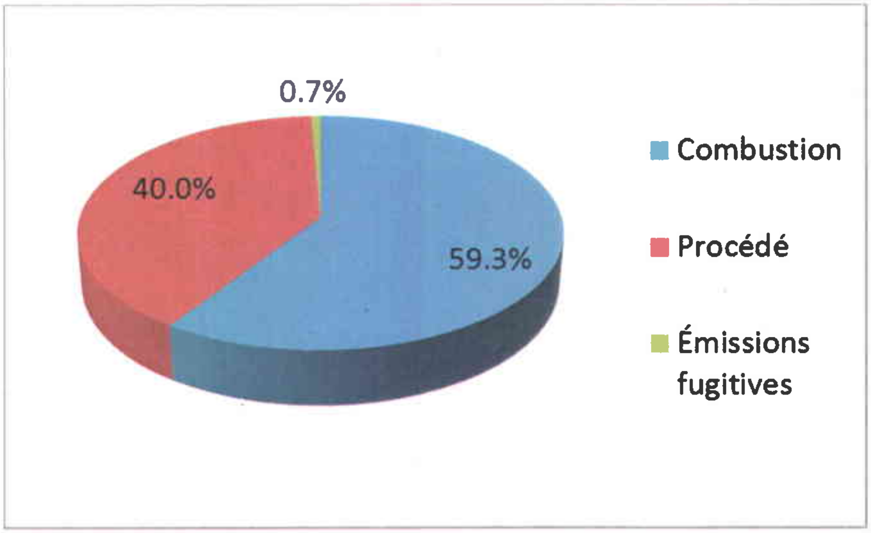

Figure 1.4 **Répartition des émissions du secteur industriel (MDDEFP, 2013)**

Les émissions résultant de la combustion regroupent les émissions issues de l'usage des combustibles fossiles pour la production, ainsi que les émissions provenant des centrales thermiques exploitées par les entreprises. Depuis 1990, les émissions issues de ce sous-secteur ont diminué de 6.7% (17.2 Mt eq. CO_2 en 1990 contre 16.1 Mt eq. CO_2 en 2010). L'amélioration de l'efficacité énergétique, ainsi que l'utilisation de substituants aux combustibles fossiles sont les principaux facteurs responsables de cette baisse. Les facteurs économiques comme la fermeture permanente ou temporaire d'usines sont également à considérer. Le Tableau 1.2 présente par ordre croissant les industries ayant les plus fortes émissions liées à l'utilisation de combustibles fossiles.

Tableau 1.2 Émissions liées à la combustion dans le secteur industriel (MDDEFP, 2013)

Industrie	Émissions (Mt éq. CO_2)
Raffineries de pétrole	3.5
Production de métaux ferreux	2.4
Pâtes et papiers	1.4
Industries chimiques	1.2
Cimenteries / Usine de chaux	0.8
Alumineries	0.4

Passons maintenant à ce qui concerne les émissions liées aux procédés, ce sous-secteur regroupe les émissions de GES comme sous-produit des procédés. Il comprend également les émissions d'hydrofluorocarbures issues notamment de la réfrigération, de la fabrication des mousses plastiques et les extincteurs d'incendies. Entre 1990 et 2010, les émissions issues des procédés ont diminuées de 17.7% (13.2 Mt éq. CO_2 en 1990 contre 10.8 Mt éq. CO_2 en 2010). Les améliorations technologiques apportées aux alumineries, ainsi que la fermeture en 2007 de la dernière usine de production de magnésium sont responsables de cette baisse. En 2010, la production d'aluminium représentait la plus grosse source de GES provenant des procédés avec 57.5% des émissions (6.2 Mt éq. CO_2). Arrive ensuite la production de minéraux non-métalliques avec 22.2% (2.4 Mt éq. CO_2), puis la production de métaux ferreux avec 6.3% (0.7 Mt éq. CO_2). Les émissions liées à la production de minéraux non-métalliques proviennent des cimenteries et des usines de chaux (2.4Mt éq. CO_2). Lors de leurs fabrications, le CO_2 est émis lors de la décomposition du carbonate de Ca. Depuis 1990, la production de ces produits a augmenté, et se traduit par une hausse de 44.4% des émissions.

1.1.1.5 Dioxyde de carbone (CO_2)

Avec un potentiel de réchauffement global (PRG) égal à 1, le CO_2 à un effet à long terme plus faible que le CH_4 ou le N_2O (respectivement 21 et 310). Cependant, le CO_2 représentait en 2004 76.7% des émissions de GES anthropiques mondiales (Figure 1.1b). La majeure partie des émissions de CO_2 sont issues de la combustion des combustibles fossiles (Figure 1.1b).

Le cycle du carbone (Figure 1.5) montre les flux entre les différents réservoirs de carbone de la planète. On distingue dans un premier temps les différents réservoirs, ici repartis dans les quatre sphères « superficielles ». Le plus important est constitué par les roches sédimentaires, suivis par les océans et, plus particulièrement, l'océan profond (+100 m de profondeur).

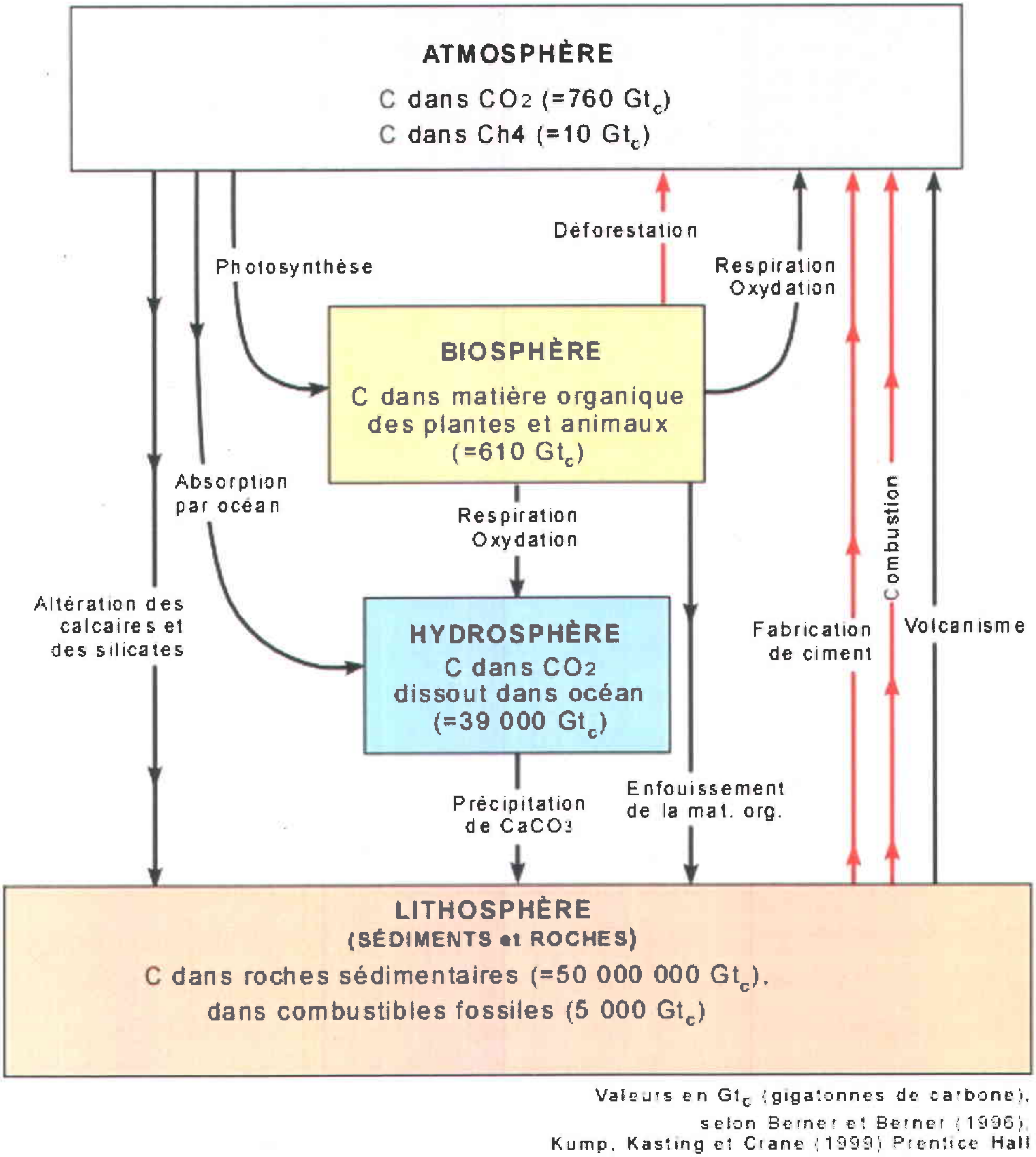

Figure 1.5 Cycle global du carbone CO_2 (Bourque, 2004)

Chacun des réservoirs communique via différents échanges. Dépendamment des flux, les temps de résidence du carbone dans chaque réservoir varient. Ainsi, le temps moyen pour un atome de carbone dans l'atmosphère est de 4 ans, de 11 ans dans la biosphère et de 385 ans dans l'hydrosphère superficielle (100 Ka dans l'océan profond) et 200 Ma dans la lithosphère (Bourque, 2004). Le cycle du carbone se divise ensuite en un cycle pour le carbone organique et le carbone inorganique. Les flèches rouges dans la Figure 1.5 représentent la contribution humaine dans le cycle. L'augmentation du CO_2 atmosphérique causée par les émissions anthropogéniques, serait responsable de changements climatiques dans les prochains siècles (IPCC, 2001, Seinfeld *et al.*, 1998). Ces changements ont également un impact sur les capacités de stockage des différents réservoirs de carbone (Cao *et al.*, 1998, Cramer *et al.*, 2001, Sarmiento *et al.*, 1996). La communauté scientifique est unanime sur le lien entre les changements climatiques est les émissions anthropiques de GES (IPCC, 2013).

Le CO_2 est un gaz contenu dans l'air. L'air est majoritairement constitué de diazote (N_2), qui représente 78.08% d'une mole d'air. On retrouve ensuite du dioxygène (O_2) qui représente 20.95% d'une mole d'air. Le taux de dioxyde de carbone contenu dans l'air varie avec le temps. D'une part, la variation annuelle est d'environ 6.5 ppmv (partie par million en volume) d'amplitude. D'autre part, le taux moyen annuel augmente de 1.2 à 1.4 ppmv par an. En 2008, on estimait à 384 ppmv (0.0384%) le taux de CO_2 de l'air. Cette valeur au début de l'ère industrielle était de 278 ppmv (Brimblecombe, 1996).

Le dioxyde de carbone, dans les conditions normales de température et de pression (298 ^{o}K, 1 atm) se présente sous forme gazeuse. Comme le montre la Figure 1.6, le CO_2 se sublime à -78.5^{oo}C à pression atmosphérique. La phase liquide, ne peut exister qu'à une pression minimale de 5.11 atm pour un intervalle de température allant de -56.6^{oo}C (point triple) à 31.1^{oo}C à 72.9 atm (point critique) (Lide, 2004). Du fait de la très forte électronégativité des atomes d'oxygène, l'atome de carbone est fortement électrophile. Le dioxyde de carbone est une molécule apolaire, mais celui-ci peut facilement se polariser sous l'action de dipôle induit. Ce dernier est donc soluble dans l'eau. Ces aspects sont détaillés au Chapitre 3.1.

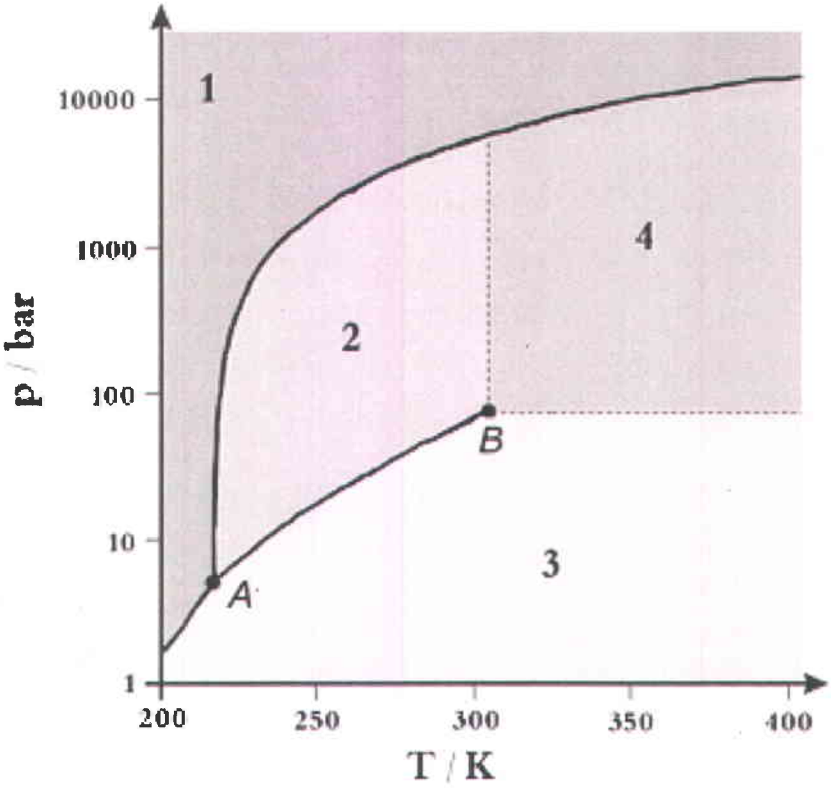

Figure 1.6 **Diagramme température pression du CO_2. 1: Phase Solide, 2: Phase liquide, 3: Phase gazeuse, 4: Fluide supercritique, A : Point triple, B : Point critique (source : Wikipedia/Wikicommons)**

Les utilisations du dioxyde de carbone sont nombreuses. On l'utilise sous forme gazeuse pour notamment l'extinction des incendies et comme composant pétillant des boissons gazeuses. Sous forme liquide, on l'emploie entre autre comme liquide réfrigérant pour congeler certains aliments et dans l'industrie électronique. On le retrouve également sous forme liquide dans les extincteurs, plus communément appelé neige carbonique. Sous forme solide, on le nomme glace carbonique ou carboglace. Il est utilisé sous différentes formes pour la congélation de produits, pour ralentir la fermentation en vinification, ou encore, pour produire une fumée épaisse comme effet spécial. Sous la forme supercritique, le CO_2 est utilisé comme solvant, qui contrairement aux autres n'est pas toxique. On l'utilise donc dans l'agroalimentaire et la parfumerie pour extraire les aromes, ou pour décaféiner le café. C'est également sous cette forme que le CO_2 est injecté dans une formation géologique en vue de sa séquestration.

1.1.1.6 Séquestration du CO_2

Ce paragraphe propose une brève description des possibles techniques de séquestration du CO_2 à partir du document de Reichle *et al.* (1999).

Séquestration dans les océans : Les océans séquestrent déjà naturellement du CO_2. L'enjeu est de pouvoir connaître l'impact d'une séquestration provoquée sur les écosystèmes et les cycles biogéochimiques des océans. Actuellement, cette option est quasiment abandonnée car les effets mesurés sur les populations marines, ainsi que les coûts engendrés sont trop élevés pour que la technologie soit rentable.

Séquestration du carbone dans les écosystèmes terrestres (sols et végétation) : Cette technique vise à augmenter la séquestration par les sols et la végétation, en augmentant la photosynthèse, en réduisant la décomposition de la matière organique (processus qui génère des GES) et en créant de l'énergie en récupérant les GES émis lors des transformations biologiques.

Séquestration géologique du CO_2 : Technologie la plus médiatisée. Une fois le CO_2 capté, celui-ci est transporté dans sa phase supercritique jusque dans une formation géologique (champs de pétrole, couches de charbon, aquifères) où il est séquestré. Les enjeux actuels, sont d'acquérir suffisamment de données pour identifier des sites, de s'assurer de la stabilité à long terme du CO_2 séquestré et, ainsi, de rassurer les populations. Les effets sismiques sont également un enjeu avec cette technique. Quelques millions de tonnes ont été séquestrés sous la mer du Nord en Norvège jusqu'à maintenant et plusieurs sites expérimentaux sont à l'étude dans le monde (Moutenet *et al.*, 2012).

Carbonatation minérale : Cette technique vise à la séquestration du CO_2 en faisant réagir le CO_2 sur des roches silicatées contenant du magnésium (Mg) ou du calcium (Ca), afin de créer des minéraux carbonates géologiquement stables.

1.1.2 Résidus miniers du sud du Québec

1.1.2.1 Géologie

Le sud du Québec est traversé par les Appalaches. Cette chaîne de montage de l'est de l'Amérique du Nord s'étend de Terre Neuve au Canada au centre de l'Alabama aux États-Unis. Ces dernières sont le résultat d'une obduction lors du renfermement de l'océan Iapetus il y a

450 M d'années et sont donc constituées de complexes ophiolitiques (Eardley, 1951). Différents métamorphismes des basaltes océaniques associés à la présence de failles ont, entre autre, entraîné la formation d'importants gisements d'amiante chrysotile et à la serpentinisation de péridotite (Équation 1.1) (Laurent, 1975).

Équation 1.1 Processus de serpentinisation de péridotite

$$2Mg_2SiO_4 + 2H_2O + CO_{2_{(g)}} \leftrightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3$$

Le chrysotile se retrouve essentiellement dans des roches ultramafiques serpentinisées de caractère ophiolitique (Hora, 1997). La présence de failles issues de zones de cisaillement est nécessaire pour la formation des veines de chrysotile (Wicks *et al.*, 1977). La gangue est constituée de brucite et de magnétite (essentiellement aux épontes). On retrouve également de l'antigorite et de la lizardite associées aux veines (Hora, 1997).

1.1.2.2 Serpentine

Cette étude vise à utiliser les résidus miniers du sud du Québec, et plus particulièrement ceux issus de la région de Thetford Mines et Asbestos. Ceux-ci ont majoritairement été générés par l'extraction de l'amiante chrysotile, bien que l'on trouve également d'anciennes exploitations de chromite, ainsi que d'autres minéraux associés aux complexes ophiolitiques. Globalement, la roche encaissante (qui constitue les résidus) est de la serpentinite. La serpentinite, est une roche qui est principalement constituée des minéraux de la famille des serpentines. Les serpentines sont des phyllosilicates (silicates en feuillets) qui comprennent également les micas, la chlorite, le talc, ainsi que les argiles. La structure générale consiste à l'empilement de couches tétraédriques (T) et octaédriques (O) (Figure 1.7) (Nelson, 2011). La couche T est constituée de cercles de six tétraèdres de SiO_4^- dont trois des quatre atomes d'oxygène sont partagés avec un autre tétraèdre. La couche octaédrique est identique à la structure de la brucite ($MgOH_2$) lorsque le cation est divalent, ou de la gibbsite si ce dernier est trivalent. Dans le cas des serpentines, on parle de phyllosilicates trioctahédriques.

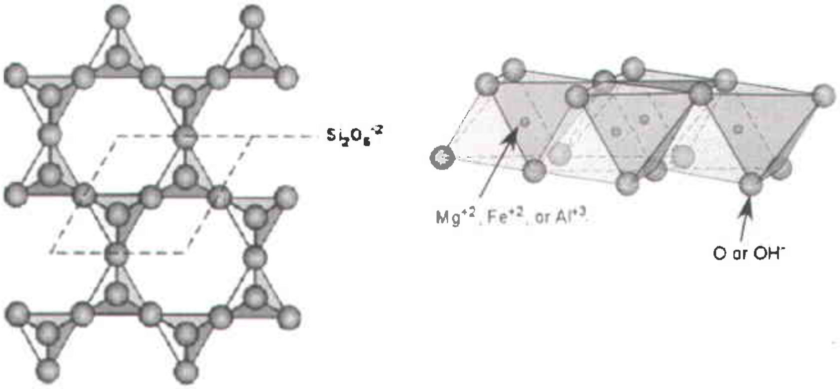

Figure 1.7 Schématisation de la couche tétraédrique (T) à gauche et octaédrique (O) à droite d'un phyllosilicate (Klein *et al.*, 1993, Nelson, 2011)

La serpentine regroupe trois différents minéraux, la lizardite, l'antigorite et le chrysotile. Tous sont caractérisés par la formule chimique $Mg_3Si_2O_5(OH)_4$. Ces derniers sont différenciés par leur structure (Figure 1.8) (Whittaker *et al.*, 1956, Wicks *et al.*, 1977). La lizardite se présente de façon plane, tandis que le chrysotile est enroulé et l'antigorite est ondulé. L'écart entre les feuillets est d'environ 7.1-7.3 Å dans le cas des serpentines (Bailey, 1988, Nagy, 1995).

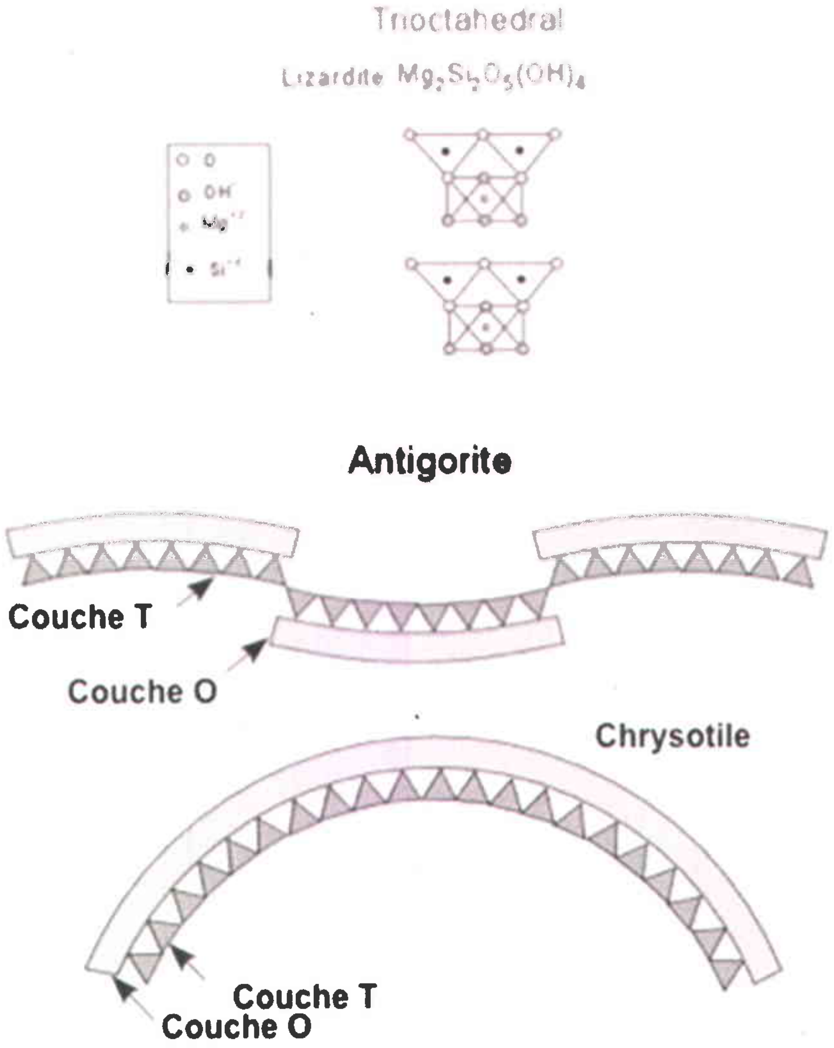

Figure 1.8 Structure de la lizardite, de l'antigorite et du chrysotile modifié d'après (Nelson, 2011)

1.1.3 Carbonatation minérale

1.1.3.1 Généralités

Le lien entre le CO_2 et les résidus miniers ultramafiques du sud du Québec est la carbonatation minérale. Les premiers travaux mentionnant la notion de carbonatation minérale sont ceux de Seifritz (1990), qui introduit l'idée de séquestrer le CO_2 en formant une liaison avec un minéral. Cette solution est directement inspirée des processus naturels ayant amené à la formation des roches carbonatées qui constituent l'un des principaux réservoirs de carbone de la lithosphère. La carbonatation minérale consiste en la réaction entre le CO_2 dissout ou non dans l'eau et une phase minérale contenant un ou plusieurs éléments bivalents, amenant à la formation des carbonates associés (Bodénan F. *et al.*, 2006). Cette forme de séquestration permet donc d'offrir un stockage du CO_2 sous une forme stable, inerte et solide. Le mécanisme général de la carbonatation est précisé par l'Équation 1.2 (Maroto-Valer *et al.*, 2005) :

Équation 1.2 **Réaction globale de carbonatation minérale**

$$(Mg,Ca)_xSi_yO_{x+2y} + xCO_2 \rightarrow x(Mg,Ca)CO_3 + ySiO_2$$

La réaction de carbonatation minérale est spontanée, naturelle et exothermique. Elle participe aux processus d'altération des roches silicatées, sur une échelle de temps très longue. C'est d'ailleurs ce dernier point qui représente l'enjeu majeur pour l'application d'un tel processus pour la réduction du CO_2 atmosphérique. Il faut en effet être capable d'accélérer la réaction, tout en évitant d'avoir recours à des méthodes énergivores, polluantes et coûteuses.

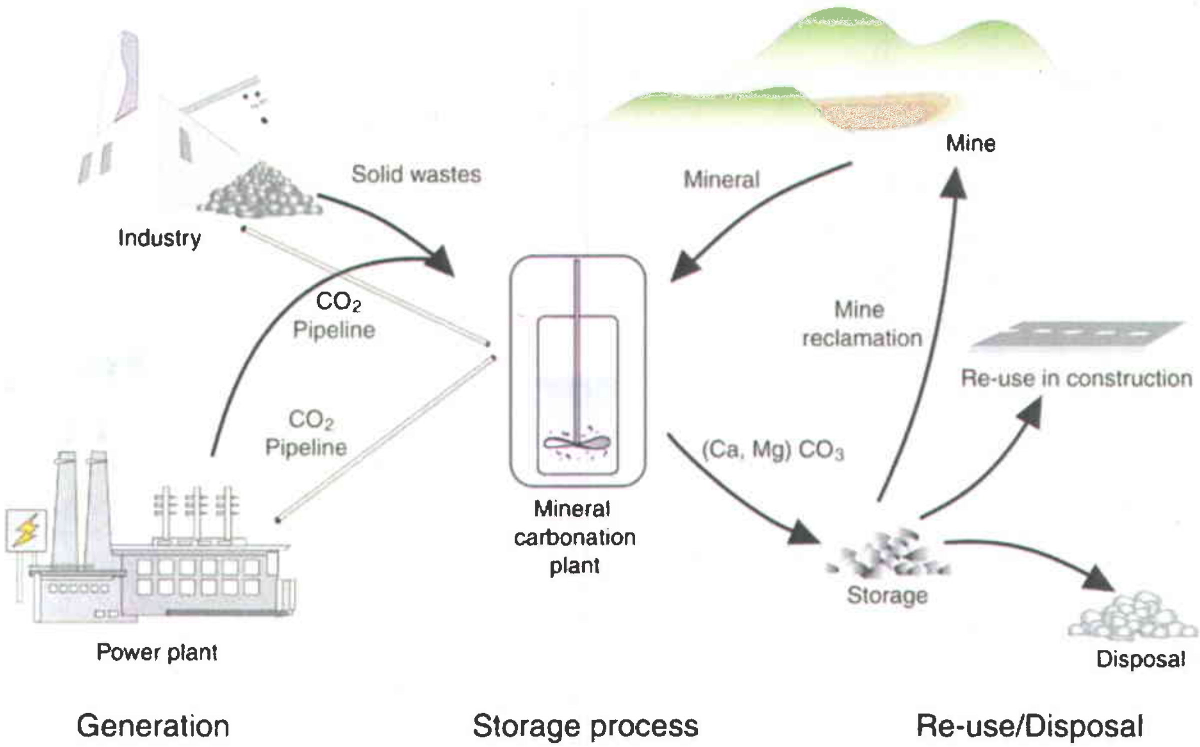

Figure 1.9 **Diagramme général de l'implantation de la carbonatation minérale comme procédé de séquestration (IPCC, 2005)**

Le diagramme présenté Figure 1.9, montre différentes possibilités pour l'utilisation de la carbonatation minérale comme processus de séquestration. L'usine de séquestration peut également être installée directement sur le site de l'émetteur, ce qui enlève la nécessité de transport du CO_2. Aujourd'hui, l'utilisation de résidus ultramafiques comme les cendres de fours à chaux, les scories ainsi que certains résidus miniers est également possible. Une fois sous forme de carbonate, le CO_2 peut être stocké en le retournant à la mine d'où est extrait le matériel réactif. Il peut également être utilisé dans divers domaines, comme réfractaire dans la sidérurgie, matériel ignifuge, agent chaulant dans le traitement de l'eau, ou encore dans le secteur pharmaceutique dépendamment de sa pureté.

1.1.3.2 Carbonatation minérale in-situ

La carbonatation minérale *in situ* s'apparente plus à la séquestration géologique. Celle-ci vise à injecter le CO_2 dans une formation géologique contenant des oxydes de Mg ou de Ca, comme les aquifères salins associés à des roches basiques (basaltes) (Kelemen *et al.*, 2011). Tout comme dans l'atmosphère, le CO_2 injecté va tendre à former des carbonates et à se stabiliser. La réaction est réalisée dans des conditions de température et de pressions élevées, ce qui permet d'augmenter la cinétique de la réaction (Kelemen *et al.*, 2008). Néanmoins, les sites de stockage doivent répondre à un certain nombre de conditions concernant les propriétés des roches, la profondeur, ainsi que les propriétés géologiques (Bachu *et al.*, 1994).

1.1.3.3 Carbonatation minérale ex-situ

A l'inverse, la carbonatation *ex-situ* vise le traitement de l'effluent gazeux en dehors de la formation géologique. Le matériel réactif est extrait et réagit avec le CO_2 dans un réacteur. Depuis les premiers travaux de Lackner *et al.* (1995) qui fit réagir des péridotites, de la serpentinite, des gabbros ou encore des basaltes en phase aqueuse à haute température, beaucoup de méthodes utilisant différents matériaux ont été étudiées.

1.1.3.3.1 Carbonatation en phase sèche

La carbonatation en phase sèche consiste à faire réagir directement le gaz avec le réactif solide à une température et une pression donnée. Cependant, l'application industrielle d'une telle réaction utilisant des minéraux naturels que les serpentinites, la wollastonite, ou encore l'olivine, est impossible dû à la lenteur de la réaction (Larachi *et al.*, 2010, Newall, 1999). À l'inverse, la réaction se déroule plus rapidement avec l'utilisation d'oxydes ou d'hydroxydes de Ca et de Mg plus réactifs (Bearat *et al.*, 2002, Butt *et al.*, 1997, O'Connor *et al.*, 2002). Cependant, la réactivité de ces matériaux les rend également moins stables dans la nature et en font des espèces plus rares (IPCC, 2005). Diverses méthodes d'extraction du Mg (ou du Ca) peuvent être utilisées afin de produire des oxydes avant la réaction de carbonatation, comme celle proposée par Nduagu (2008) qui prévoit l'extraction du Mg de matériaux silicatés par des sels d'ammonium, suivi de la précipitation de $Mg(OH)_2$ favorisée par la présence de cations (issus du silicate). L'utilisation de déchets alcalins comme les poussières de fours de cimenterie, de fonderie, des scories ou les cendres d'incinérateur ayant une forte teneur en oxydes de Ca et de Mg ont également démontré une bonne efficacité de conversion dans des conditions sèches (Baciocchi *et al.*, 2006, Bobicki *et al.*, 2012, Huijgen *et al.*, 2005, Huntzinger *et al.*, 2009). La réaction en phase gazeuse démontre également une meilleure économie d'énergie comparativement à la réaction en phase aqueuse (Zevenhoven *et al.*, 2008). Cependant, les conditions de température (entre 200 et 500°C) nécessaires pour l'obtention de taux de carbonatation raisonnables sont très élevées et représentent un frein majeur à l'utilisation d'un procédé de carbonatation de type gaz-solide.

1.1.3.3.2 Carbonatation minérale en phase aqueuse

Alors que la réaction dans les conditions sèches demande des matériaux spécifiques, ou encore des conditions de températures très élevées, la réaction en phase aqueuse permet l'extraction du matériel actif suivi de la précipitation des carbonates associés (Équation 1.3) (IPCC, 2005).

Équation 1.3 Série de réaction mise en jeux lors de la carbonatation minérale en phase aqueuse. a) dissolution du CO_2, b) dissolution du solide, c) précipitation du carbonate

$$CO_{2_{(g)}} + H_2O \leftrightarrow H_2CO_{3_{(aq)}} \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad \text{a)}$$

$$Ca/Mg\,silicate + 2H^+ \leftrightarrow (Ca/Mg)^{2+} + SiO_2 + H_2O \qquad \text{b)}$$

$$(Ca/Mg)^{2+} + HCO_3^- \leftrightarrow (Ca/Mg)CO_{3_{(s)}} + H^+ \qquad \text{c)}$$

Les premiers travaux de carbonatation en phase aqueuse visent à fournir une méthode de séquestration. Le CO_2 est donc dans un premier temps capturé via un procédé de capture (comme les amines), puis ensuite acheminé vers l'usine de séquestration (Figure 1.9). Les travaux publiés par les groupes de recherche américains du Los Alamos National Laboratory (LANL) et de l'Albany Research Center (ARC) font office de pionniers d'un point de vue de la carbonatation minérale en conditions aqueuses. Dans un premier temps, les études se sont majoritairement intéressées à quatre minéraux issus de roches ultramafiques, l'olivine, les serpentines, la lizardite, l'antigorite et la wollastonite pour leur disponibilité (Goff *et al.*, 2000). Les conditions de température et de pression appliquées sont aux alentours de 185°°C et 150 atm (O'Connor *et al.*, 2001). Celles-ci sont élevées mais en dessous de celles rapportées dans les conditions sèches. Les rendements rapportés varient dépendamment du matériel utilisé avec respectivement 91% et 34% de carbonatation pour l'olivine et la serpentine en 6 h. La wollastonite est bien plus réactive et offre 82% de carbonatation après 1 h (Huijgen, 2003). L'ajout de sels, tels que NaCl et $NaHCO_3^-$, permet d'augmenter les rendements de carbonatation notamment grâce au maintien de la solution de réaction à un pH neutre, et à l'ajout de HCO_3^- en solution qui favorise la précipitation des carbonates (Chen *et al.*, 2006). Néanmoins, d'importantes limitations d'ordre cinétique réduisent l'efficacité de la réaction. En effet, la dissolution du matériel solide est trop lente, et souvent limitée par l'accumulation de silice non réactive (passivation layer) (Béarat *et al.*, 2006). L'enjeu est donc de trouver un moyen d'augmenter la dissolution du matériel solide. Dans le cas des serpentines, l'ajout d'une activation thermique permet de doubler les rendements et d'obtenir 83% de carbonatation en 1 h (O'Connor *et al.*, 2005). De plus, diverses méthodes sont proposées afin d'augmenter la dissolution. Parmi elles, l'utilisation d'acide sulfurique semble être la plus efficace afin d'augmenter la lixiviation des cations (Alexander *et al.*, 2007, Maroto-Valer *et al.*, 2005). Néanmoins, la précipitation des carbonates n'est pas favorisée dans une solution acide, et une rectification du pH est nécessaire (Park *et al.*, 2004). Cependant, les coûts globaux engendrés par le prétraitement du solide représentent une entrave majeure à l'application d'un procédé de carbonatation minérale pour la réduction des émissions de CO_2 (Gerdemann *et al.*, 2007). En ce sens, la recherche s'est tournée vers des matériaux alternatifs aux minéraux naturels, comme les poussières de four à chaux, de cimenteries (Huntzinger *et al.*, 2009), d'aciéries ou d'incinérateur (Rendek *et al.*, 2006), ainsi que d'autres déchets alcalins comme les bétons résiduels (Katsuyama *et al.*, 2005), les scories (Bonenfant *et al.*, 2008) ou les résidus miniers. Ces derniers présentent l'avantage d'être déjà extraits (plus de frais liés à l'extraction) et peuvent dans certains cas avoir une granulométrie fine (réduction ou enlèvement des étapes de broyage) (Bobicki *et al.*, 2012). Enfin, l'utilisation de résidus comme matériel de carbonatation, se présente comme une méthode de gestion de déchets valorisante et utile d'un point de vue environnemental. La réactivité dépend du matériel et des conditions utilisées (cf Tableau 1.3). Enfin, la quasi-totalité de références discutées jusqu'à présent s'intéressent à la réaction d'un gaz concentré en CO_2. Seul les travaux d'une équipe de recherche de l'École Polytechnique Fédérale (ETH) de Zurich mentionne le traitement direct d'un gaz de cheminée sans capture et préconditionnement (Werner *et al.*, 2011). Cependant, à cause de limitations liés à la saturation de la solution les rendements de carbonatation de la serpentine traitée thermique sont limités à 20% (Werner *et al.*, 2013).

1.1.3.3.3 Carbonatation minérale dans les conditions atmosphériques

La réaction de carbonatation minérale s'inscrit dans le cycle géochimique du carbone. L'étude de la réaction dans les conditions atmosphériques se présente dans un premier temps comme un moyen d'évaluation et de quantification des flux du cycle. Cependant, dans le cas des résidus miniers ultramafiques, d'importantes quantités de CO_2 sont séquestrées naturellement par des résidus d'anciennes exploitations de chrysotile notamment (Huot *et al.*, 2003, Wilson *et al.*, 2006). Les travaux de Wilson *et al.* (2009) ont démontré que la carbonatation de résidus d'une dizaine d'années s'élevait à 0.3%. Récemment, de nombreux travaux se sont penchés sur les moyens de quantification et de compréhension de la dynamique de carbonatation des haldes. La composition des résidus, ainsi que la granulométrie, tout comme pour la réaction en réacteur impacte grandement sur la réactivité des résidus (Assima *et al.*, 2013, Pronost *et al.*, 2011). D'un point de vue géodynamique, la fréquence des précipitations et la saturation en eau des résidus jouent un rôle important (Assima *et al.*, 2012). Au niveau de la dissolution des résidus, et plus particulièrement de la brucite, l'augmentation de la pression partielle de CO_2 permet d'accélérer la libération du Mg de la structure du minéral, grâce à l'augmentation de la concentration de ligands dû à la dissolution du CO_2 dans l'eau interstitielle (Harrison *et al.*, 2012). Ces mêmes auteurs mettent en évidence une sous-évaluation de la vitesse de dissolution de la brucite dans les conditions atmosphériques, et rapportent que 22 à 57% des émissions issues de l'activité d'une mine pourraient être séquestrée. L'utilisation de résidus miniers comme moyen de séquestration du CO_2 atmosphérique semble être intéressante, mais la nécessité d'importantes modifications des terrils pour optimiser entre autre la carbonatation du cœur des tas reste problématique. La voie biologique est également une possibilité afin d'améliorer la cinétique et l'efficacité globale de carbonatation des résidus (Power *et al.*, 2010, Power *et al.*, 2013).

1.1.3.4 Applications industrielles de la carbonatation minérale

Différentes approches ont été envisagées afin de mettre au point un procédé efficace. Les principales variantes rapportées dans la littérature sont présentées au Tableau 1.3. On distingue deux méthodologies; un traitement dit direct, où la réaction se déroule dans une seule unité, ou un traitement en plusieurs étapes. Les procédés directs sont dans les deux cas réalisés avec un gaz 100% CO_2 à haute température et haute pression, et ont été jugés non viables économiquement (Gerdemann *et al.*, 2007). L'alternative présentée par les procédés en deux ou trois étapes avec extraction des cations par lixiviation en milieu acide offre l'avantage de pouvoir réduire le coût des conditions de carbonatation. Cependant, l'ajout de base pour ramener le pH dans des conditions basiques ainsi que la régénération des acides/base représente un inconvénient majeur. Les travaux de l'ETH se rapprochent de la méthodologie présentée dans cette étude. Le gaz de type de combustion est traité dans un premier réacteur dans des conditions de basse température et de basse pression afin de lixivier le Mg de la serpentine. La pulpe est ensuite amenée dans un second réacteur où la température est augmentée afin de précipiter les carbonates sous une légère pression partielle de CO_2. Néanmoins, le faible taux de conversion limite l'applicabilité du procédé présenté.

La carbonatation minérale a déjà fait l'objet de nombreuses études et les principaux obstacles économiques et pratiques à une application industrielle sont connus. Actuellement, le prétraitement thermique de serpentine en vue d'une utilisation pour la capture et la séquestration est breveté (WO 2011/035047 A2). Le brevet WO 2008/142017 A2 mentionne l'utilisation de phyllosilicates comme matériel de séquestration du CO_2 contenu dans un gaz de combustion. Ce dernier utilise la chaleur fournie par le gaz pour le prétraitement suivi d'une carbonatation directe. Il ne s'agit donc pas d'une réaction en phase aqueuse, car l'eau est ici produite lors de la déshydratation du matériel et par la vapeur d'eau contenue dans le gaz. Enfin, le brevet US 7,919,064 B2 décrit l'utilisation de déchets alcalins comme matériel de capture et de séquestration du CO_2 contenu dans un gaz de combustion. Le résidu est ici mélangé dans une solution aqueuse contenant du carbonate de sodium. L'application, WO2010/097451 A2, présente un procédé de séquestration de CO_2 issu d'un gaz de combustion par contact direct du gaz préalablement refroidis, avec une solution contenant des phyllosilicates (serpentines) activés thermiquement suivant l'application WO2010/097444 A1 à basse température. Les carbonates sont par la suite précipités à 120°C sous atmosphère de CO_2.

Tableau 1.3 Principaux procédés de carbonatation minérale en phase aqueuse rapportés dans la littérature

Auteurs	Matériel	Conversion de CO_2	Temps de réaction (min)	Temp. (°C)	Pression (bar)	Taille des particules & pulpe	Prétraitement	Remarques
<u>Procédés directs</u>								
O'Connor et al., (2005)	Olivine	49.5%	60	185	152	≤38 µm	Traitement thermique pour la serpentine	Procédé direct avec ajout de 0.64 M $NaHCO_3$ et 1 M NaCl sauf pour Wollastonite (eau distillée)
	Serpentine	73.5%		155	116	150 g/L		
	Wollastonite	81.8%		100	40			
Huijgen et al., (2007)	Wollastonite	75%	30	200	20	≤38 µm		Procédé direct sans additifs
	Scories	69%				200 g/L		
<u>Procédés multi-étapes</u>								
Yamasaki *et al.* (2001)	Wollastonite	Ratio de cristallisation 10%	10	60	30	20 µm	Extraction à l'acide acétique à 60°C pendant 60 min	Carbonatation d'acétates de Ca
Park *et al.* (2004)	Serpentine	65%					Dissolution dans un mélange d'acide phosphorique et oxalique et EDTA à 70°C	Les conditions de réaction entre le gaz et le Mg dissout sont floues. Rectification du pH avec NaOH ou NH_4OH
Teir *et al.* (2009)	Serpentinite	3.1 t pour capter 1 t CO_2		30	Atm.	74-125 µm	Extraction à 70°C avec HNO_3 ou HCl	Rectification du pH avec NaOH. Production d'hydromagnésite avec gaz 10% CO_2.
Kodama *et al.* (2008)	Silicates de Ca Scories	80%	60	50	-		Extraction avec NH_4Cl à 80°C production de $CaCl_2$	Réaction avec un gaz de combustion (13% de CO_2) en présence de NH_3. Calcite précipitée à 80°C à partir de la solution obtenue $(NH_4)_2CO_3$ $CaCl_2$
(Werner *et al.* (2013))	Serpentine	20%	120	30-90	0.1 et 1 pCO_2	≤125 µm 50-200 g/L	Serpentine traitée thermiquement	Réaction entre la serpentine et le gaz type gaz de combustion puis précipitation dans une seconde unité à 90°C avec pCO_2 = 0.1 bar

1.1.4 Principes réactionnels

La réaction de carbonatation simplifiée en phase aqueuse de la serpentinite est représentée par la réaction ci-dessous (Équation 1.4):

Équation 1.4 Réaction simplifiée de la serpentine en phase aqueuse

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 + H_2O \rightarrow 3MgCO_3 + 2SiO_2 + 3H_2O + 64kJ/moles$$

Celle-ci peut se diviser en trois étapes :

- Dissolution en solution du CO_2;
- Lixiviation du Mg du résidu;
- Précipitation des carbonates de Mg.

1.1.4.1 Solubilité du CO_2

La solubilité peut être déterminée en utilisant la loi de Henry qui énonce que la pression partielle d'un gaz *i* est égale au produit de la constante de Henry par la concentration du gaz *i* en solution (Équation 1.5).

Équation 1.5 Loi de Henry

$$p_i = k_H \times C_i$$

L'Équation 1.5 met en évidence que la pression influence la solubilité du gaz. Ainsi, plus la pression augmente, plus la solubilité augmente. Dans le cas du CO_2, l'équation s'exprime selon (Stumm *et al.*, 1996) :

Équation 1.6 Expression de la solubilité du CO_2

$$p_{CO_2} = k_H \times [H_2CO_3^*]$$

où $[H_2CO_3^*]$ représente la concentration totale en CO_2 dissout selon :

Équation 1.7 Expression de la concentration totale de CO_2 dissout

$$[H_2CO_3^*] = [CO_2] + [H_2CO_3]$$

Ces aspects sont détaillés dans le chapitre 2.

Tableau 1.4 Valeurs de la constante de Henry pour le CO_2, le N_2 et l'O_2 à 298.15°K d'après *Chemistry webook from the NIST*

Gaz	CO_2	N_2	O_2
$k°_H$ (mol.kg^{-1}.bar^{-1})	0.035	0.00065	0.0013
d(ln(k_h))/d(1/T) (K)	2400	1300	1500

Les constantes de Henry présentées au Tableau 1.4 montrent que le CO_2 est nettement plus soluble que l'oxygène et le diazote. Ceci est explicable par la présence de liaisons covalentes π, qui induisent une forte polarité. De ce fait, la molécule est plus facilement soluble dans l'eau.

La constante de Henry diffère en fonction de la tëmpérature. Celle-ci peut-être recalculée grâce à l'Équation 1.8.

Équation 1.8 Expression de la constante de Henry en fonction de la température

$$k_H(T) = k_H \times e^{\frac{d(lnk_H)}{d(1/T)} \times \frac{(1/T)-1}{298.15}}$$

D'après cette réaction, plus la température augmente, plus k_H diminue et, par conséquent, la solubilité diminue également.

1,1.4.2 Équilibre du CO_2 dissout

Le dioxyde de carbone se dissout dans l'eau en suivant plusieurs étapes :

Équation 1.9 Équilibre calco-carbonique

$$\boldsymbol{CO_{2_{(g)}} \leftrightarrow CO_{2_{(aq)}}} \qquad \text{(a)}$$

$$\boldsymbol{CO_{2_{(aq)}} + H_2O \leftrightarrow H_2CO_3} \qquad \text{(b)}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad \text{(c)}$$

$$\boldsymbol{HCO_3^- \leftrightarrow CO_3^{2-} + H^+} \qquad \text{(d)}$$

Dans un premier temps, le CO_2 au contact de l'eau passe de la forme gazeuse à la forme aqueuse (a). S'en suit la formation d'acide carbonique (b). Ensuite l'acide carbonique libère un proton pour former l'ion bicarbonate (c), puis l'ion carbonate (d). Le pH de l'eau gouverne les réactions (c) et (d). Ainsi, la dissolution du CO_2 entraine une diminution du pH, mais un pH élevé est nécessaire pour déplacer l'équilibre vers la droite pour les réactions (c) et (d). Les constantes d'équilibre pour les différentes espèces carbonatées sont présentées au Tableau 1.5.

Tableau 1.5 Constantes d'équilibres d'après Stumm *et al.* (1996)

Constante	**Valeur à 25°C et 1 atm**
$K_H = [H_2CO_3^*]/p_{CO2}$	29.41 mol/L/atm
$K = [CO_{2(aq)}]/[H_2CO_3]$	650
$K_1 = ([HCO_3^-]^*[H^+]) / [H_2CO_3^*]$	4.5×10^{-7}
$K_{H2CO3} = K_1 + K_1K$	2.92×10^{-4}
$K_2 = ([CO_3^{2-}]^*[H^+]) / [HCO_3^-]$	4.7×10^{-11}

La Figure 1.10 présente les espèces carbonatées en solution à l'équilibre pour une température de 25°C et pour C_T= 0.01 mol/L en fonction du pH, avec $C_T = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$.

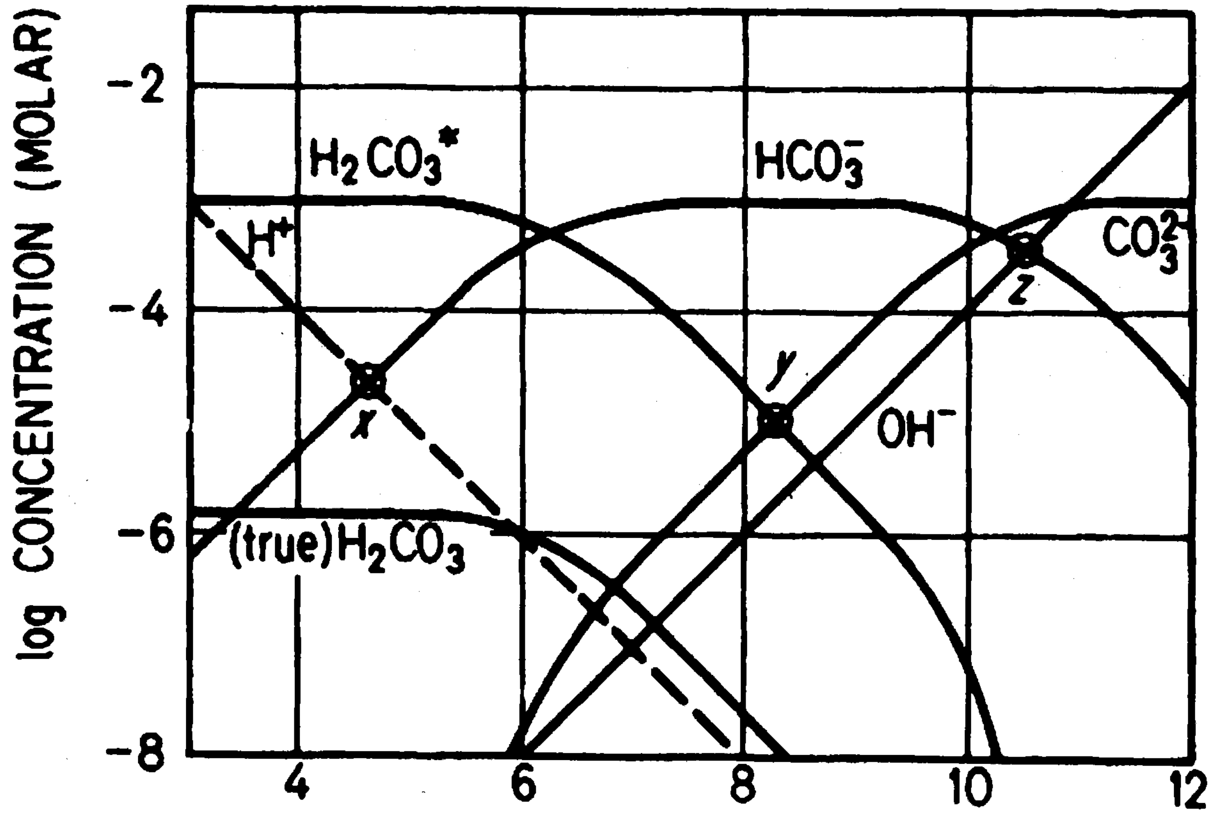

Figure 1.10 **Diagramme d'équilibre des phases carbonatées dans une eau naturelle à 25°C (Stumm *et al.*, 1996)**

L'équilibre entre les différentes espèces carbonatées est dépendant du pH. À 25°C, pour un pH inférieur à 4.4, l'espèce prédominante est le CO_2. À pH = 6.34 (pK_1), le CO_2 et l'ion bicarbonate sont à concentrations égales. Il en est de même pour l'ion bicarbonate et l'ion carbonate à pH 10.33 (pK_2). Lorsque le pH est supérieur à 12.1, l'espèce prédominante est le CO_3^{2-}.

1.1.4.3 Dissolution du résidu minier

La disponibilité en Mg^{2+} dans la phase aqueuse est dépendante de la dissociation du résidu. Cette étape est donc limitante quand à la formation de carbonates.

D'un point de vue général, la composition chimique de la surface du minéral contrôle le taux de dissolution des phyllosilicates (Nagy, 1995). Tous les groupements hydroxydes ou oxydes présents à la surface du minéral sont des sites potentiels pour l'adsorption des protons ou des ligands et il est admis qu'il n'existe pas de différence de potentiel d'adsorption entre l'extrémité et le reste de la surface des fibres dans le cas de chrysotile (Bales *et al.*, 1985).

Le mécanisme de dissolution peut-être simplement décrit par les modèles de réduction de particules avec ou sans changement de taille (shrinking core model) (Levenspiel, 1998). La réaction ici intervient dans un premier temps à la surface de la particule. La zone de réaction se déplace par la suite vers le noyau. Les matériaux inertes (résidus/poussières) ainsi que les produits sont soit laissés en place ou détachés de la surface (Figure 1.11).

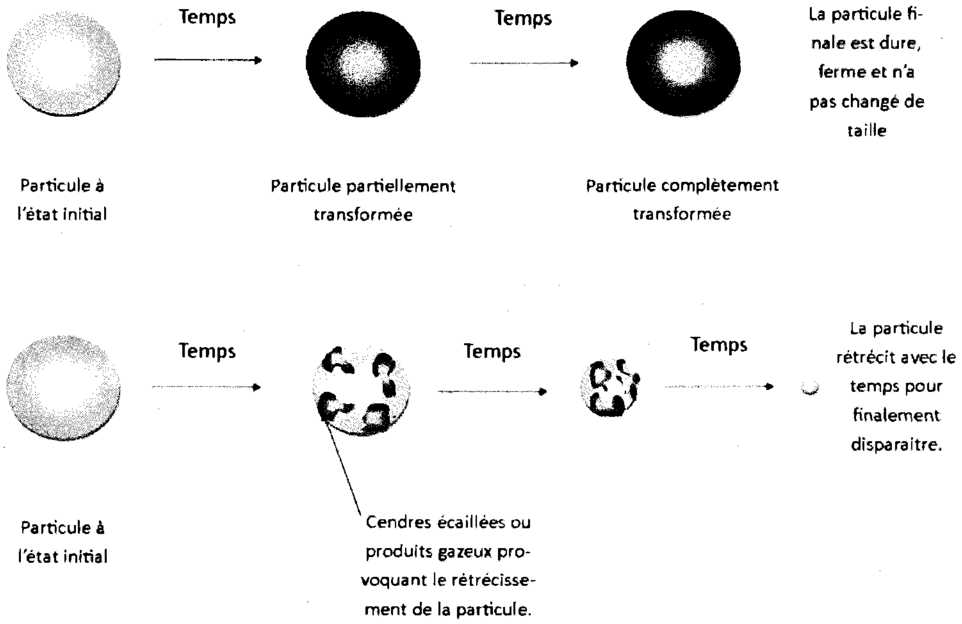

Figure 1.11 **Représentation schématique du modèle de réduction de particules sans ou avec rétrécissement (Levenspiel, 1998)**

La cinétique de dissolution des serpentines peut-être contrôlée par des phénomènes de diffusion, comme par exemple le transport des réactifs à travers la surface du minéral ou encore à travers la couche de résidus dans le cas d'une réduction sans changement de taille. Dans ce cas, l'équation cinétique suit une loi parabolique (Équation 1.10 a). Alternativement, la dissolution peut être contrôlée par des phénomènes de surface et la vitesse de réaction suit ici une loi d'ordre zéro (Équation 1.10b). Dans certains cas, la dissolution peut être contrôlée par l'effet conjoint des deux phénomènes.

Équation 1.10 Loi cinétique décrivant une dissolution contrôlée par (a) des phénomènes de transport et (b) de surface (Stumm *et al.*, 1996)

$$r = \frac{dC}{dt} = k_p t^{-1/2} \; (M.s^{-1}) \qquad \text{(a)}$$

$$r = \frac{dC}{dt} = Ak \; (M.s^{-1}) \qquad \text{(b)}$$

D'un point de vue général, l'augmentation du pH réduit le taux de relargage du Mg, tandis que celui de la silice semble être favorisé à un pH plus élevé (Bales *et al.*, 1985). L'ensemble des mesures expérimentales des taux de dissociation pour les serpentines à 25°C en fonction du pH disponibles dans la littérature est présenté à la Figure 1.12. Cipolli *et al.* (2004), à partir des observations de Luce *et al.* (1972) et de Bales et Morgan (1985), proposent l'Équation 1.11 pour les mécanismes de dissolution acide des serpentines à 25°C:

Équation 1.11 Expression de la loi cinétique de dissolution des serpentines en fonction du pH

$$\log r \; (mol.m^{-2}.s^{-1}) = 0.70pH - 6.38$$

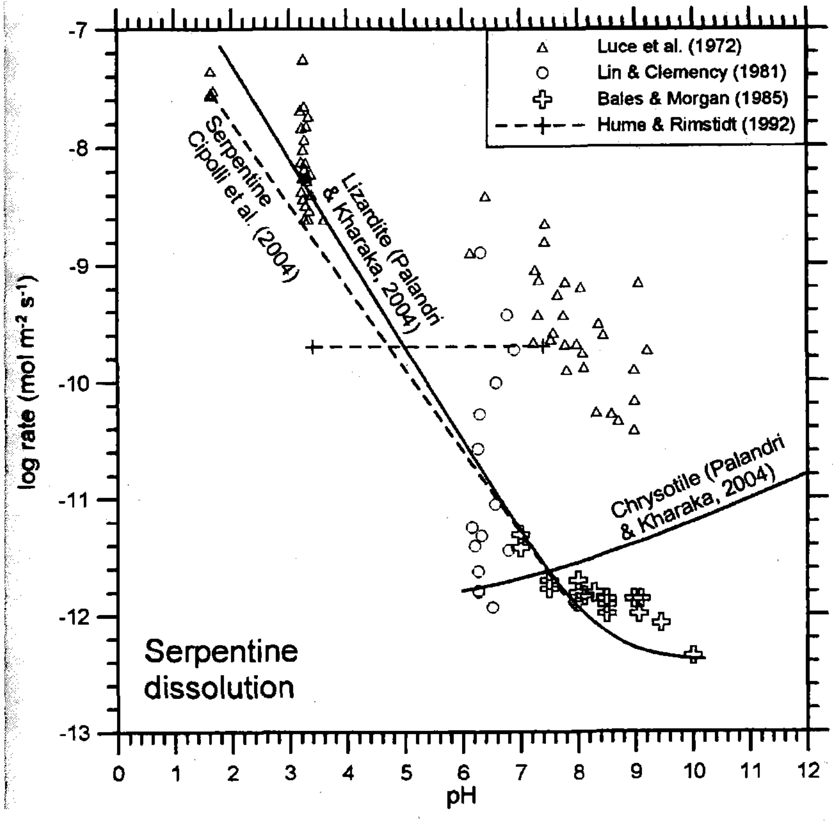

Figure 1.12 **Taux de dissociation des serpentines en fonction du pH (Marini, 2007)**

La dissolution des serpentines peut être représentée par la réaction suivante (Équation 1.12) (Stumm *et al.*, 1996):

Équation 1.12 **Réaction de dissolution d'une serpentine et formation de silice hydratée**

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2SiO_2.H_2O + 3H_2O\ K_c = 1.374 \times 10^{-70}$$

La constante d'équilibre K_c montre que la réaction tend vers la gauche. La formation de silice amorphe est de ce fait très peu probable. À contrario, la dissolution de la serpentine amenant à la formation de dioxyde de silice est plus probable thermodynamiquement (Équation 1.13)[1].

Équation 1.13 Réaction de dissolution de la serpentine formation de silice

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2SiO_2 + 5H_2O \; K_c = 1.831 \times 10^{32}$$

1.1.4.4 Précipitation des carbonates de magnésium

Le dernier aspect de la carbonatation minérale en phase aqueuse est la précipitation des carbonates de Mg. Le système $MgO\text{-}CO_2\text{-}H_2O$ est un système complexe du fait de la grande variété de formes de carbonates hydratés qui peuvent se former. Les principales formes de carbonates de Mg sont présentées au Tableau 1.6.

Tableau 1.6 Principaux carbonates de Mg et leurs énergies de formation de Gibbs d'après Hänchen et al. (2008)

Minéraux	Formules	$\Delta G°_f$ (kJ/mol)
Magnésite	$MgCO_3$	-1027.83
Nesquehonite	$MgCO_3.3H_2O$	-1723.95
Lansfordite	$MgCO_3.5H_2O$	-2199.20
Artinite	$MgCO_3.Mg(OH)_2.3H_2O$	-2568.62
Hydromagnésite	$(MgCO_3)_4.Mg(OH)_2.4H_2O$	-5864.66

Le carbonate le plus stable pour une large gamme de température et de pression partielle de CO_2 est la magnésite (Christ *et al.*, 1970), mais sa formation à température ambiante est impossible et seule la nesquehonite peut précipiter à faible température et faible pression partielle de CO_2

---

[1] Valeurs calculées grâce au logiciel HSC 7.0 (Outotec).

(Hänchen et al., 2008). Le Tableau 1.7 présente les différentes formes en fonction de la température.

Tableau 1.7 Carbonates de Mg formés en fonction de la température d'après Hänchen et al. (2008)

Température (°C)	Minéraux
25-40	Nesquehonite
40-100	Hydromagnésite
60-200	Hydromagnésite/Magnésite

D'un point de vue cinétique, la précipitation des carbonates hydratés est favorisée par le caractère hautement hydraté du Mg^{2+}. Le cation Mg^{2+} possède en effet de fortes couches dipolaires d'eau. On dénombre six molécules d'eau pour la première couche et 12 sur la seconde, sachant que seule la deuxième couche peut être modifiée par des changements de température ou de concentration (Burgess, 1978). Par exemple, l'activité de l'eau peut être réduite en ajoutant du NaCl et ainsi limiter la couche hydratée sur le Mg^{2+} (Christ *et al.*, 1970). D'un autre côté, le rayon ionique des ions carbonates est beaucoup plus grand. De ce fait, la molécule de CO_3^{2-} n'est pas complètement entourée d'eau, ce qui facilite son adsorption à la surface des cristaux (Hänchen *et al.*, 2008). De plus, Hänchen et al. (2008) avancent qu'un faible ratio Mg^{2+}/CO_3^{2-} peut contribuer à maintenir les molécules d'eau éloignées du cristal.

1.1.4.5 Prétraitement thermique du résidu

Les caractéristiques thermiques de la serpentine sont obtenues par les analyses thermogravimétriques (TGA) et montrent une perte majeure du poids aux alentours de 600°C, dû à la déhydroxilation du cristal. La présence d'un changement de poids entre 400 et 500°C traduit la présence de brucite (Nagamori *et al.*, 1980). Les analyses différentielles thermiques (DTA) confirment les observations de TGA. Un premier pic endothermique entre 400 et 500°C pour la présence de brucite. S'en suit un deuxième endotherme (entre 650 et 700°C) plus important que le premier qui définit la déhydroxilation de la serpentine. À partir de 800°C, un pic exothermique apparaît et montre une recristallisation du minéral en enstatite (Bearat *et al.*, 2002, Nagamori *et al.*, 1980). La décomposition thermique de la serpentine est représentée par l'Équation 1.14. Le mécanisme présenté pour la chrysotile est également applicable aux autres minéraux de la famille des serpentines (Figure 1.13).

Lors de la déhydroxilation de la serpentine, une forme amorphe de serpentine est observée, appelée meta-serpentine (McKelvy *et al.*, 2006). Cette phase amorphe est chimiquement active, du fait de la disponibilité du Mg et de la Si (Nagamori *et al.*, 1980). En effet, l'éclatement de la structure cristalline, permet une meilleure solubilité du Mg. L'activation chimique de la serpentine est augmentée lorsque le minéral est finement broyé, ce qui diminue la pression partielle de vapeur d'eau, car elle peut se diffuser plus facilement. Une faible concentration en vapeur d'eau évite en effet la recombinaison du Mg et de la silice dans le cristal (Nagamori *et al.*, 1980). Li *et al.* (2009) ont observé de meilleurs rendements de carbonatation après prétraitement à 650°C pendant 30 min.

Équation 1.14 Réaction de déhydroxilation de la serpentine, formation d'olivine (forsterite)

$$Mg_3Si_2O_5(OH)_4 \rightarrow Mg_2SiO_4 + MgSiO_3 + 2H_2O$$

Chrysotile hydratée avec excès de brucite	$Mg_3Si_2O_5(OH)_4 . xH_2O . yMg(OH)_2$
	$-xH_2O \ \downarrow$ 100-250 °C
Déshydratation de la brucite	$Mg_3Si_2O_5(OH)_4 . yMg(OH)_2 \ \dashrightarrow$
	$-yH_2O \ \downarrow$ ~400°C
Déshydratation de la chrysotile Anhydre	$Mg_3Si_2O_5(OH)_4 + yMgO$
	$-4H_2O \ \downarrow$ 600-780°C
	Mg_3Si_2O
	$\downarrow$ 810°C
Forsterite, Silice	$3\ Mg_2SiO_4 + SiO_2 \ \dashrightarrow$
	$\downarrow$ >1000°C
Forsterite, Enstatite	$2\ Mg_2SiO_4 + MgSiO_3$

Figure 1.13 **Réactions thermiques de déhydroxilation des fibres de chrysotile (Jolicoeur *et al.*, 1981)**

1.1.5 Hypothèses et originalité

La revue de la littérature montre que la carbonatation minérale à fait l'objet de nombreuses études. Différentes conditions et méthodologies ont été étudiées afin de contourner les limitations de la réaction. Néanmoins, l'utilisation de la carbonatation comme moyen de réduction des émissions de CO_2 n'a pas été démontrée comme économiquement viable. Les coûts engendrés par le préconditionnement du matériel ajouté aux faibles taux de conversion se présentent encore comme les principaux inconvénients de la réaction. Néanmoins, il ressort de la littérature un manque d'études dans des conditions similaires à celle retrouvées dans l'industrie. En effet, les émissions gazeuses industrielles sont généralement liées à la production d'énergie par la combustion d'énergies fossiles. Au final, aucune industrie ne rejette un gaz concentré en CO_2 et la nécessité d'une étape de capture et de purification du gaz représente une entrave économique majeure. Ainsi, en travaillant avec un gaz proche de celui émis par une industrie simplifie le schéma du procédé et pourrait réduire les coûts. Par ailleurs, la présence d'importantes quantités de résidus miniers dans le sud du Québec à une distance raisonnable de grands émetteurs est une opportunité non négligeable. Enfin, certains coûts de préconditionnement comme le broyage et le traitement semblent inévitables du fait de l'importance de ces étapes sur la réactivité du matériel.

L'hypothèse suivante est posée : Il est possible de mettre au point un procédé plus simple permettant d'enlever environ 80 % du CO_2 d'un gaz de cheminée contenant environ 18 % de CO_2 et qui peut permettre d'obtenir un carbonate de magnésium ayant une valeur significative pour l'industrie ce qui offrirait la possibilité d'avoir une valeur ajoutée et de donner un bilan économique positif au procédé.

Les objectifs de cette étude sont :

- Vérifier la réactivité des résidus miniers du sud du Québec avec un gaz dont la composition est proche de celui émis par une cimenterie;
- Optimiser les paramètres opératoires afin d'obtenir un taux d'enlèvement du CO_2 élevé et une bonne conversion du solide (carbonatation) tout en offrant un procédé faisable et viable industriellement;

- Favoriser la précipitation de carbonates de Mg purs dans une étape subséquente. Ce produit ayant une valeur marchande.

1.2 MÉTHODOLOGIE

1.2.1 Matériel et dispositif réactionnel

Le principal résidu minier utilisé pour cette étude provenait de l'ancienne exploitation de chromite, American Chrome située à Coleraine. Ce résidu se présentait sous une forme grossière et a donc été dans un premier temps concassé avant d'être broyé à l'aide d'un broyeur à disque (*Bleuler-Mill, NAEF*) afin d'obtenir un matériel ayant une granulométrie inférieure à 75 µm avec une moyenne de 28µm (Figure 1.14). La taille des grains a ensuite été déterminée à l'aide d'un granulomètre Laser (*Horiba LA-950V2, Laser Scattering Particules Size Distribution Analyzer*). Dépendamment des conditions expérimentales, le résidu a été traité thermiquement dans une fournaise (*Furnatrol 133, Thermolyne Sybron Corporation*).

Figure 1.14 **Illustration du résidu sous sa forme brute, après concassage puis après broyage**

Le dispositif réactionnel utilisé pour la carbonatation minérale est schématisé à la Figure 1.15. La réaction a été réalisée dans un réacteur *Mini bench top reactor 4560* de *Parr Instrument Company®* à tête fixe. Après réaction, le gaz a été échantillonné dans un sac de type *Tedlar Bags* de 3.8 L doté d'une valve *on/off*. La concentration en CO_2 du gaz a ensuite été mesurée par un analyseur de CO_2, *Quantek Instruments®, modèle 906*. Le résidu obtenu après réaction a, quant à lui, été filtré et séché dans une étuve à 60°C. Les carbonates de Mg ont été précipités à partir de la solution riche en Mg et en C dissout dans bécher agité à environ 40°C.

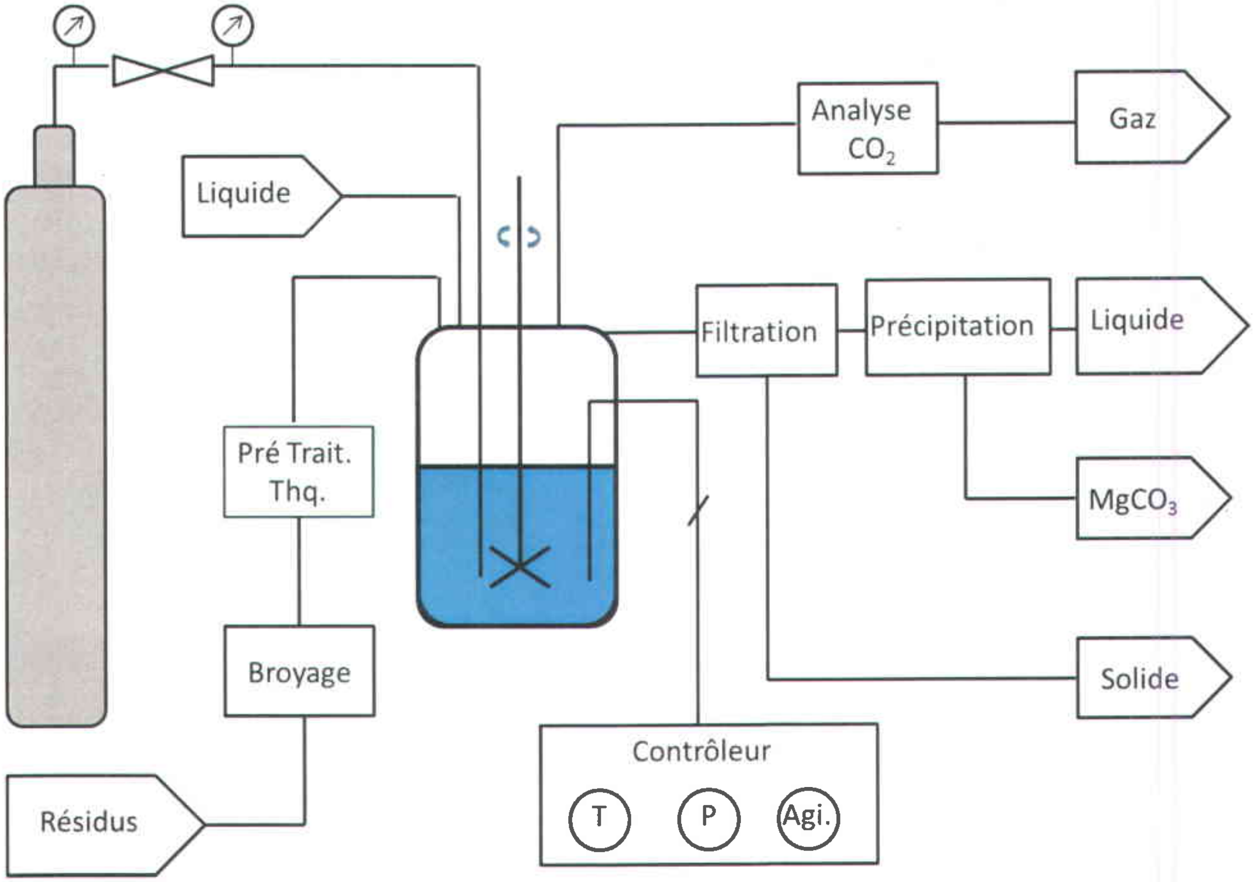

Figure 1.15 **Schéma du dispositif réactionnel**

1.2.2 Paramètres suivis

La séparation solide et liquide en fin de réaction a été effectuée par filtration sous vide sur des membranes *Whatman 934-AH* de 1.5 µm de porosité. Les éléments (Ca, Co, Cr, Cu, Fe, Mg, Ni et Si) contenus dans les résidus ont été mesurés par ICP-AES (*modèle Vista AX CCO Simultaneous ICP-AES, Palo Alto, CA, États-Unis*) après fusion alcaline au métaborate de lithium (méthode Claisse). Des contrôles de qualité ont été effectués en analysant des échantillons de roches certifiés (W2, BCR2, BHVO2 fournis par le *US Geological Survey* et SARM1, SARM5 du *National Institute for Metallurgy*, ZAF). Les éléments majeurs de la solution ont également été analysés à l'ICP-AES. Le carbone inorganique dissout a, quant à lui, été mesuré au TOC-V CPH (*Shimadzu, Tokyo, Japon*).

1.2.3 Caractérisation du résidu

1.2.3.1 Granulométrie

Les résultats de l'analyse granulométrique du résidu brut sont présentés au Tableau 1.8. La granulométrie fine a été obtenue en réalisant deux cycles de broyage successifs. La surface spécifique rapportée par le granulomètre est estimée. Des mesures de l'échantillon au BET ont établi la surface à 21.6 m^2/g. La différence entre les deux valeurs est dû au fait que le granulomètre calcule la surface spécifique en considérant toute les particules comme sphérique. La mesure réalisée au BET est donc plus précise.

Tableau 1.8 Analyse granulométrique de l'échantillon brut après broyage

Echantillon	**Taille médiane (µm)**	**Taille moyenne (µm)**	**Surface spécifique estimée (m^2/kg)**
a	10.8	30.4	7362
b	10.0	27.8	9457
c	10.1	27.0	7860
Moyenne	10.3 ± 0.5	28.4 ± 1.8	8226 ± 1094

1.2.3.2 Composition chimique

La composition chimique du résidu est présentée au Tableau 1.9. Le Mg et la Si sont majoritaires ce qui coïncide avec la composition chimique d'une roche de serpentinite. La présence de fer peut s'expliquer par la substitution du Mg dans la structure des serpentines (Hora, 1997). De même que les résidus sont issus d'une ancienne mine de chrome, la chromite contient également du fer. Il est à noter que la teneur en calcium est très faible tout comme le carbone inorganique. Une perte au feu de 11.6% est en accord avec les valeurs rapportées dans la littérature.

Tableau 1.9 **Caractérisation chimique du résidu**

Éléments	Unités	Valeur
Al_2O_3	wt%	1.6
CaO	wt%	0.04
Cr_2O_3	wt%	0.9
Fe_2O_3	wt%	19
MgO	wt%	47
MnO	wt%	0.05
SiO_2	wt%	42
C_{inorg}	wt%	0.24
LOI [a]	wt%	11.6

1.2.3.3 Analyse DR-X

Le diffractogramme du résidu brut est présenté en Annexe 1. Les principales phases d'une serpentinite sont présentes. Il est cependant impossible de distinguer l'une d'une autre sur cette analyse. Néanmoins, l'analyse visuelle de l'échantillon permet d'identifier la lizardite comme principale phase minérale. Aucune fibre de chrysotile n'est également visible sur l'échantillon. La présence de chromite et de magnétite est également vérifiée.

1.2.3.4 Analyse au MEB

La Figure 1.16 présente les images prises au microscope électronique à balayage (MEB) (*modèle ZEISS EVO 50, Oberkochen, Allemagne*) en électrons rétrodiffusés. Un échantillon de poudre est figé dans une résine, puis poli afin d'obtenir une coupe des grains. On peut remarquer les points très clairs qui représentent des grains de chromite ou de magnétite (M). On peut également noter la présence d'inclusions de chromite/magnétite (flèches rouge) dans des grains de serpentine (S) De plus, sur certains grains, on note la présence de zones plus sombres (flèches vertes), montrant la variation de composition de la serpentinite.

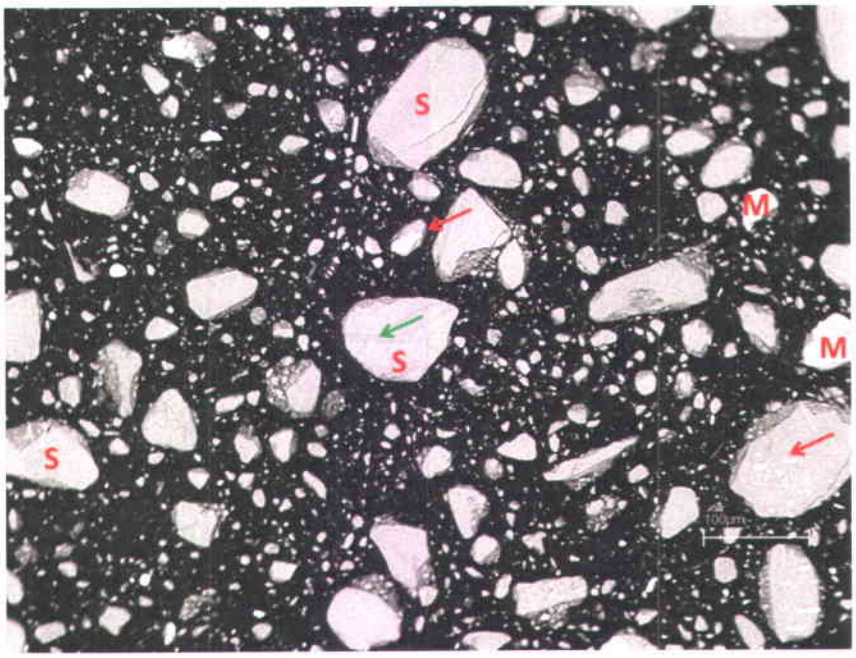

Figure 1.16 **Image en électrons rétrodiffusés d'une surface polie du résidu brut (x500)**

1.2.4 Mode opératoire

Les résidus préalablement pesés ont été introduits dans la cuve du réacteur. Un volume d'eau a été ajouté dépendamment de la densité de pulpe voulue. Le pH de la solution a ensuite été mesuré, puis le réacteur fermé. L'agitation est par la suite mise en route et fixée à 600 rotations par minute (rpm), puis le gaz a été introduit. Afin de ne pas diluer le gaz avec l'air présent dans la cuve, la vanne de sortie a été laissée ouverte pendant environ 5 sec avant d'être fermée. Une fois la pression désirée atteinte, la valve d'entrée du gaz est fermée. Il est à noter que la pression n'était pas maintenue constante et que celle-ci diminuait au cours de la réaction dû au passage du CO_2 en phase liquide. Lors de la réaction, la température, la pression et l'agitation ont été suivies et enregistrées à l'aide d'un enregistreur (*ParrCom*). Une fois le temps de réaction terminé, le gaz a été échantillonné à l'aide d'un sac de type *Tedlar Bag®*, puis analysé via l'analyseur de CO_2. Le réacteur a été rapidement dépressurisé lors de l'échantillonnage du gaz afin de stopper la réaction. Le résidu a ensuite été filtré. Une partie du liquide a été gardée pour l'analyse du C_{inorg} dissout. Un autre aliquote a été acidifié par 0.5% de HNO_3 pour analyse à l'ICP-AES. Le restant était soit conservé ou utilisé pour des essais de précipitation. Le résidu solide a été séché à 60 °C, puis le C_{inorg} a été analysé au CHNS. Le reste de l'échantillon solide a également été analysé à l'ICP-AES. Des analyses complémentaires au MEB, DRX TGA ont également été réalisés sur certains échantillons.

1.3 Principaux résultats

1.3.1 Optimisation des paramètres opératoires

1.3.1.1 Essais préliminaires

Dans un premier temps, les essais en laboratoire ont visé la validation et l'optimisation de la réaction dans diverses conditions de température et de pression. L'effet du traitement thermique a également été évalué. Les premiers essais visaient à reproduire les conditions opératoires développées par l'ARC (150°°C, 116 bar, 1 M NaCl et 0.64 M $NaHCO_3$ pendant 1 h). Lors des essais, aucune chute de pression n'a été observée. Ceci s'explique par la différence de pression partielle de CO_2. Comme mentionné, la solubilité du CO_2 dans l'eau dépend à la fois de la température et de la pression partielle (loi de Henry). La plus faible pression partielle de CO_2 induite avec l'utilisation d'un gaz contenant 18% de CO_2 empêche d'atteindre l'état supercritique. Il apparait donc impossible d'opérer à haute température avec une faible pression partielle de CO_2. En ce sens, les essais ont par la suite été réalisés à température ambiante (21 ± 5°°C).

L'effet de la pression globale est également explicable en regardant l'expression de la loi de Henry (Équation 2.2). Ainsi, une pression globale élevée induit une plus grande pression partielle de CO_2 et une plus grande solubilisation de CO_2. Néanmoins, opérer à haute pression implique des coûts d'opération élevés (compression du gaz, équipements spéciaux). De plus, en raison du dispositif expérimental, une pression minimale de 10.5 bar doit être utilisée afin d'avoir suffisamment de gaz en fin de réaction pour pouvoir échantillonner le gaz de façon adéquate.

Enfin, l'ajout de sels préconisé par l'ARC afin de maintenir le pH de la solution neutre, et d'augmenter la saturation de la solution pour favoriser la précipitation des carbonates ne s'applique plus. Les conditions plus douces permettent de maintenir le pH supérieur à 6 après réaction. En effet, le résidu étant basique, ce dernier tamponne l'acidification attribuable à la dissociation du CO_2 dans la solution. De plus, la précipitation dans le réacteur n'est pas désirée, car une étape de séparation des carbonates du résidu non réagit serait problématique. Le but étant d'obtenir un carbonate pur après la réaction entre le gaz et la pulpe, ce dernier est précipité à partir de la solution obtenue après filtration de la pulpe. La régénération des sels est également problématique. Il a donc été décidé d'opérer sans apport externe de sels.

1.3.1.2 Optimisation des paramètres opératoires (en batch)

Le détail des essais réalisés pour l'optimisation dans la densité de pulpe, du ratio volume de gaz sur volume de liquide et du temps de réaction sont discutés dans le chapitre 3. Ces paramètres sont extrêmement importants d'un point de vue économique. En effet, le transport de matériel solide représente un coût majeur. Il faut donc avoir un taux de conversion en carbonate le plus élevé possible afin de réduire les quantités de solides nécessaires pour le traitement du gaz.

L'optimisation des paramètres opératoires a démontré que le meilleur enlèvement de CO_2 ainsi que la plus grande quantité de Mg était lixiviée avec une densité de pulpe de 15%, un ratio volume de gaz/volume de liquide de 3.0 après 15 min de réaction en batch à une pression de 10.5 bar et à température ambiante (Tableau 1.10).

Tableau 1.10 Efficacité du CO_2 traité et du Mg lixivié pour le traitement d'une batch de 15 min

Perte Gaz	Entrée (g CO2)	Sortie (g CO2)	CO_2 traité (g CO2)	CO_2 traité (%)	Mg lixivié (%)
RT 151	0.82	0.09	0.73	89%	7.5%
RT 152	0.78	0.08	0.70	89%	7.0%
RT 153	0.81	0.11	0.70	87%	6.6%
Moyenne	0.80 ± 0.02	0.09 ± 0.01	0.71 ± 0.02	88 ± 1%	7.1 ± 0.5%

Bien que la quantité de CO_2 enlevée soit importante, la quantité de Mg lixivié reste faible avec seulement 7% du Mg contenu dans le résidu passé en solution. Celle-ci doit être augmentée car en supposant que la totalité du Mg passé en solution soit transformée en carbonates, ce dernier équivaut au taux de conversion du solide. En augmentant la pression partielle de CO_2, la dissolution du résidu est augmentée. Cependant, tel que mentionné auparavant, augmenter la pression globale n'est pas désirable. Un scénario de recirculation, basé sur des temps de résidence adaptés pour le gaz, le liquide et le solide a donc été élaboré.

Des essais successifs de batch de gaz ont été réalisés et ont démontré que la réaction était limitée par la saturation de la solution en Mg et C dissout. Ainsi, il a été décidé de remplacer la phase liquide de façon régulière. Alors que la dissolution du CO_2 dans la phase liquide est rapide, la cinétique de dissolution du résidu est plus lente. En contactant, deux batch de gaz de 15 min chaque, les rendements de Mg lixivié ont pu être doublés, tout en gardant un enlèvement de CO_2 supérieur à 80%. Tout en changeant la solution à chaque deux batch de gaz, un total de 12 batch a été traité avec le même résidu (Figure 1.17).

Tableau 1.11 Récapitulatif de l'efficacité de traitement de douze batches de gaz et de la lixiviation de Mg du résidu

Batch de gaz	CO_2 traité (g CO_2)	Mg lixivié (%)
1	0.68 ± 0.06	
2	0.69 ± 0.02	14 ± 1
3	0.67 ± 0.02	
4	0.61 ± 0.03	14 ± 1
5	0.56 ± 0.04	
6	0.41 ± 0.06	11 ± 2
7	0.44 ± 0.05	
8	0.59 ± 0.05	15 ± 1
9	0.53 ± 0.02	
10	0.42 ± 0.01	7 ± 1
11	0.27 ± 0.01	
12	0.29 ± 0.01	4 ± 1
Total	6.14 ± 0.36	64 ± 7

Après 6 batch de gaz traité, l'efficacité du CO_2 traité ainsi que la lixiviation du Mg était réduite voire nulle. En effet, la formation d'une couche passive de silice à la surface des grains limite la disponibilité du Mg et, par conséquent, sa lixiviation. Plusieurs traitements physico/chimiques ont été essayés sur le matériel solide afin de le réactiver. La meilleure solution s'est avérée d'effectuer un nouveau broyage, ainsi qu'une autre activation thermique. Ainsi, six autres nouvelles batch de gaz ont pu être traitées pour atteindre 64% de lixiviation du Mg, et une efficacité cumulée de 62.5% sur le traitement du CO_2 (Tableau 1.11). Au final, un ratio g de CO_2 traité / g de résidus de 0.55 (6.14 gCO_2 pour 11.25g de résidu) a été obtenu. Il est à noter que ce ratio est supérieur au ratio théorique calculé à partir de la stœchiométrie pour la serpentine est de 0.43. Ceci s'explique par le fait qu'une partie du CO_2 est simplement dissout et n'est pas lié à un Mg. À l'inverse, si l'on considère le Mg lixivié, le ratio est de 0.28 (64% de 0.43).

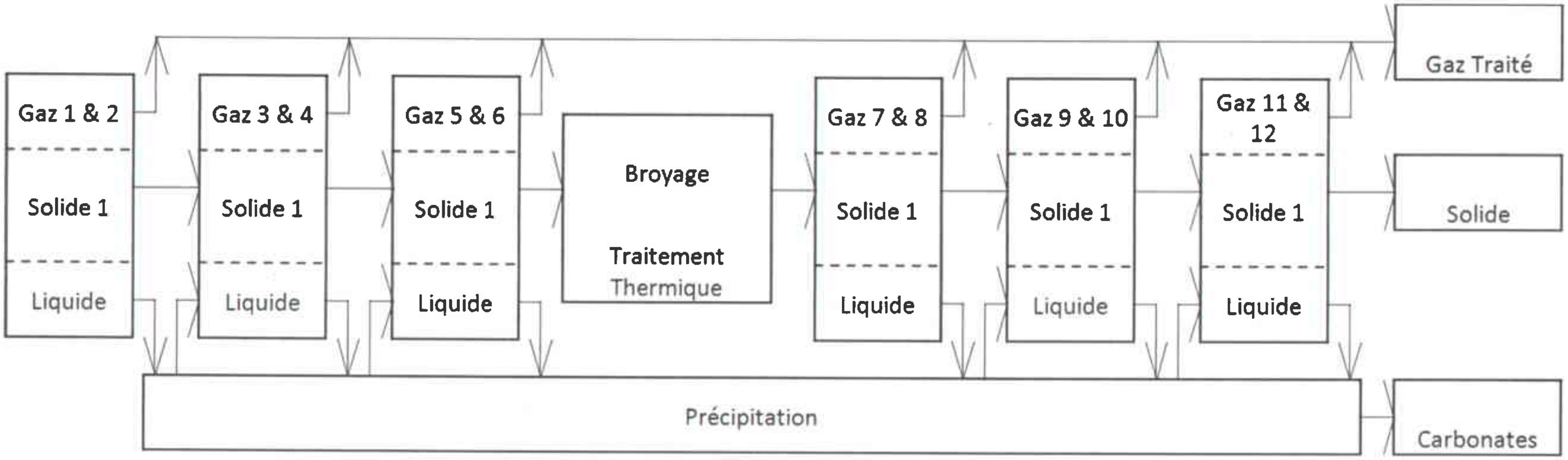

Figure 1.17 **Schéma du procédé pour le traitement de 12 batches de gaz par le même solide**

1.3.2 Mécanismes réactionnels

Les mécanismes réactionnels sont détaillés dans le chapitre 2. Lors de l'optimisation des paramètres, il a pu être mis en évidence l'importance de la pression partielle de CO_2. En effet, celle-ci gouverne la quantité de CO_2 introduite dans le réacteur, la quantité de CO_2 solubilisé. De plus, l'effet de la présence de CO_2 dissout sur la lixiviation de Mg a également été mis en avant.

En effet, la concentration de carbone inorganique dissout augmente avec la pression partielle de CO_2. En comparant les concentrations de Mg en solution avec les concentrations de carbone inorganique, une relation linéaire apparaît (Figure 1.18).

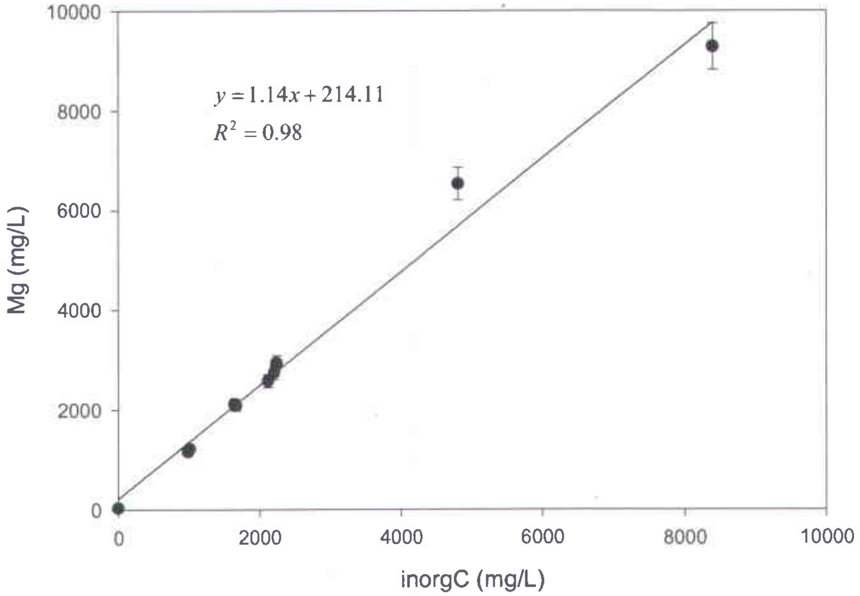

Figure 1.18 **Concentration de Mg en solution en fonction du Cinorganique dissout pour des essais à différentes pressions. Les barres d'erreur représentent une erreur de 5%**

Cette relation met en évidence le mécanisme de dissolution du résidu. Le CO_2 une fois en solution se dissout en ion bicarbonate (majoritaire dans les conditions de pH). Ces ions vont par la suite aller se lier avec le Mg, ou d'autres cations, afin de créer un complexe ($MgHCO_3^+$) à la surface des résidus. Ces complexes vont par la suite se détacher pour passer en solution. Ce sont ces mêmes complexes qui finiront par précipiter en carbonates. La cinétique de la dissolution du résidu a également été mesurée et évaluée à 3.55×10^{-11} moles/cm^2/sec. En comparaison avec les valeurs rapportées dans la littérature, ce taux de dissolution semble être compétitif avec l'utilisation d'acides forts, ou encore des sels organiques.

Comme mentionné précédemment, le taux de dissolution de la silice est plus faible que celui du Mg. De ce fait, une couche de silice apparaît à la surface des grains à mesure que le Mg passe en solution. Cette couche passive limite la disponibilité du Mg et implique des phénomènes de diffusion pour les ligands HCO_3^-. L'étude de surfaces polies de grains après plusieurs batches de gaz a permis d'identifier la présence de cette couche de matériel « non réactif » à la surface des grains de serpentine (Figure 1.19).

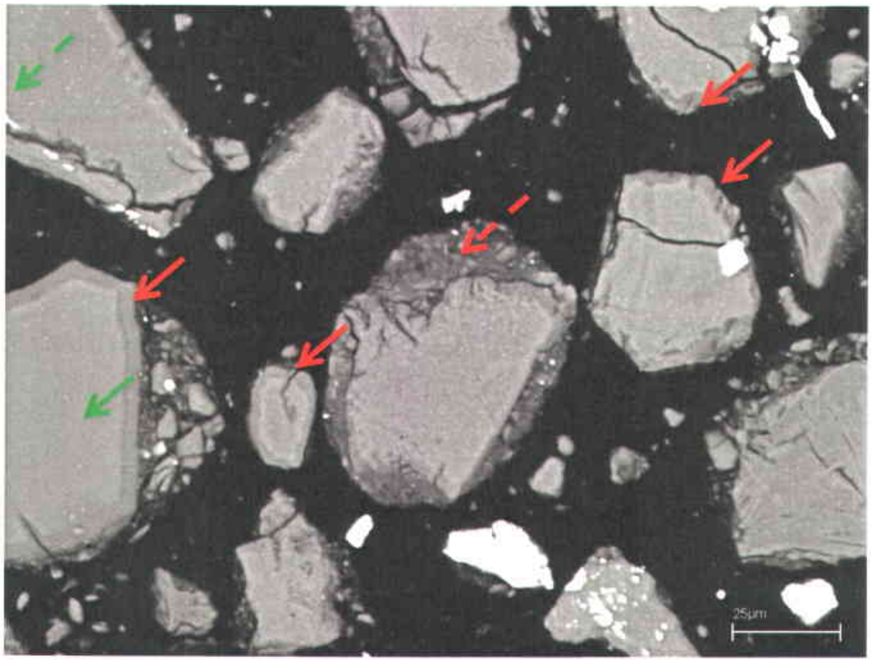

Figure 1.19 **Image MEB d'une surface polie présentant des grains après 12 batch de gaz traité**

La variation de teinte de gris entre le centre du grain plus clair (flèche pleine verte) et les bords plus foncés (flèche pleine rouge) montre la variation de composition. Ces variations ont été vérifiées par analyse EDS, ou la surface présente un pourcentage de Mg plus faible que le cœur du grain. On peut également remarquer la présence d'une couche matériel ayant réagi et étant agglomérée sur un grain dans lequel se trouve des grains plus clairs n'ayant pas réagi (flèche coupée rouge). Cet amas peut être un ensemble de particules ayant complètement réagi et aggloméré à la surface du grain ou alors traduire d'une réaction moins homogène à la surface de certains grains par rapport aux zones identifiées par une flèche rouge pleine. Enfin, le centre des certains grains présente de petits points blanc (flèche coupée verte). L'apparition de ces points de magnétite/chromite au centre du grain peut également traduire une évolution de la composition.

La dernière étape de la réaction est la précipitation des carbonates. Toutes les 2 batches de gaz traitées, la solution est filtrée. Celle-ci est majoritairement constituée de Mg et de CO_2 dissout, avec un pH compris entre 6.5 et 7.5. Ce dernier varie en fonction du nombre de batch de gaz traités par le solide. En effet, la quantité de Mg dissout diminue au fur et à mesure du traitement, réduisant l'effet tampon par rapport à l'acidification induite par la dissociation du CO_2. Le CO_2 est donc majoritairement sous la forme de HCO_3^- De plus au vue des observations faites précédemment, la concentration de Mg est directement liée à la concentration de carbone inorganique dissout mesurées dans la solution. Au moment ou la solution est filtrée (ndlr, après 30 minutes), il peut-être statué que les complexes $MgHCO_3^+$ sont majoritaires. De plus les conditions de saturation d'un point de vue de la magnesite ($MgCO_3$) sont satisfaites. La précipitation des carbonates est donc ici contrôlée par la cinétique, et celle-ci doit-être accélérée afin de satisfaire un temps de rétention raisonnable d'un point de vue industriel. En accord avec la loi d'Arrhenius, l'augmentation de la température permettras d'accélérer la réaction de précipitation. Cette dernière ne doit pas être trop fortement augmentée pour limiter le relargage du CO_2 sous forme de gaz. Cependant, la réalisation de la précipitation dans une cuve fermée avec une légère pCO_2 peut accélérer la précipitation (Hänchen *et al.*, 2008). Des essais réalisés à 40°C avec une légère agitation, ont démontrés que 63% du Mg initialement présent en solution était précipité après 3 heures. Les carbonates précipités sont ici sous forme de nesquehonite ($MgCO_3 . 3H_2O$) (Annexe 3).

1.3.3 Analyse économique

Les aspects économiques tiennent une part importante dans cette étude. L'utilisation d'un modèle de calcul des coûts a permis d'évaluer les différents facteurs ayant le plus d'impact sur le coût de procédé. Le détail de ces travaux est présenté dans le chapitre 4.

Le modèle de calcul est basé sur la capacité de traitement de l'usine, ici, la quantité de roches par heure. La quantité de CO_2 traitée par une tonne de roche est évaluée en utilisant le bilan massique obtenu à partir des résultats expérimentaux. À partir de ce même bilan de masse, et en suivant le schéma de procédé, l'ensemble des équipements est dimensionné. Le coût d'achat et de transport des équipements est évalué en utilisant le *Chemical Engineering Plant Cost Index (CPCI)*. Les coûts en capitaux sont ensuite estimés en utilisant les facteurs de Lang (Perry *et al.*, 2008). Les coûts de main d'œuvre sont calculés à partir de facteurs rapportés dans la littérature pour l'opération des différents équipements (Peters M.S. *et al.*, 1991, Ulrich G.D., 1984). Les paramètres généraux et de marché sont présentés au Tableau 1.12. L'analyse économique a été réalisée en évaluant différents scénarios faisant varier le mode de transport pour acheminer les résidus jusqu'à l'usine (camion ou train) et le type d'énergie utilisé pour le traitement thermique du résidu (gaz naturel ou biomasse).

Le bilan en GES du procédé a également été établi en marge de l'analyse économique. Ce dernier est calculé en utilisant les données énergétiques des équipements. L'énergie totale est par la suite multipliée par le facteur d'émission en CO_2 équivalents (2.0 g CO_2/kWh pour l'électricité). Dans le cas de l'activation thermique, dans le cas où la source d'énergie est le gaz naturel, un facteur de 206 g CO_2/kWh s'applique. Dans le cas où l'énergie est fournie par la biomasse, le facteur d'émission est nul étant donné qu'il s'agit de biomasse résiduelle. Enfin, le facteur d'émission pour le transport est respectivement de 0.0175 g CO_2/t.km et 0.204 g CO_2/t.km pour le train et le camion. L'évaluation des émissions totales de CO_2 liées au procédé permet de calculer la capacité nette de séquestration du procédé.

Tableau 1.12 Paramètres généraux et de marché utilisés pour l'analyse économique

Paramètres généraux du procédé		
Période d'opération	350	jours/an
Capacité	200	t roche/heure
Période d'opération journalière	24	heure/jour
Efficacité globale de l'usine	90	%
Paramètre de marché		
Taux d'inflation annuel	2.0	%/an
Taux d'intérêt annuel	2.0	%/an
Taux d'escompte annuel	8.0	%/an
Taux d'imposition sur les revenus	30	%
Taux de change	1.00	$US/$Can
Chemical Engineering Plant Cost Index	568.3	1 mars 2013

Le détail des coûts de procédé pour un scénario de base où le résidu est transporté par train et le traitement thermique est réalisé en utilisant du gaz naturel, est présenté au Tableau 1.13. L'efficacité de traitement du gaz de l'usine est de 62% (basé sur les résultats obtenus au laboratoire). L'importance du transport des résidus dans le bilan économique est bien mis en évidence. Ici, les coûts de transport présentés sont associés à l'utilisation du train. Dans le cas où le résidu serait transporté par camion, le coût serait de 59.18 \$/t CO_2 traité. Les coûts engendrés par l'activation thermique (énergie) est également important lorsque le gaz naturel est sélectionné. À l'inverse, l'utilisation de la biomasse réduit le coût à 8.94 \$/t CO_2 traité. Le coût total en capitaux pour une usine ayant une capacité de traitement de 200 t de résidu à l'heure est évalué à 182.4 M$CA. Les calculs de flux monétaires prévoient une période de retour sur investissement de 3.77 ans avec un profit net actualisé (NPV) de 236.2 M$CA pour une période de 10 ans. La profitabilité du procédé est ici assurée par les revenus générés par la vente des carbonates de Mg. En effet la production d'un carbonate pur à 95% permet d'estimer son prix de vente à 100 $/t. Cette valeur est en plus conservatrice comparativement au prix du marché évalués entre 200 et 350 $/t (Kramer A.D., 2001Kramer A.D., 2001).

Outre le revenu généré par le carbonate de Mg, la taxe carbone apporte également un produit au capital, ainsi que les possibles revenus de vente de la fraction magnétique extraite du résidu avant son utilisation.

Le bilan énergétique et en GES du procédé met en avant l'impact du prétraitement du résidu, qui représente également la plus grande source de GES émis par le procédé (Tableau 1.14). Il est à préciser que l'utilisation de camions comme mode de transport représente une imputation de 10% de la capacité de séquestration du procédé. Alors que les émissions fugitives liés au transport peuvent-être difficilement traités, celles liés au traitement thermique pourrait être séquestrée, soit par le procédé en mélangeant le gaz issu de la combustion du gaz naturel à celui de l'usine (ce qui induirait une réduction de la capacité de traitement du gaz de cheminée de l'usine) ou en ajoutant un autre procédé avec une capacité de traitement adapté aux émissions liées au traitement thermique. À l'inverse, l'utilisation de biomasse permettrait d'annuler les émissions liées à l'activation thermique et permettrait d'avoir un procédé avec une capacité de séquestration nettement plus intéressante. De plus, les revenus liés à la taxe carbone seraient également supérieurs ce qui augmenterait la profitabilité du procédé.

Tableau 1.13 Bilan des coûts et des revenus d'opération

Catégorie		**$ / tCO_2 traité**
Coûts direct d'opération		
Main d'œuvre		1.58
Utilités :		
Électricité		9.58
Eau de procédé		0.01
Énergie	*Gaz Naturel*	16.58
Chargement des résidus		5.56
Transport des résidus	*Train*	33.25
Maintenance	*2.00 % capital/an*	5.43
Cout matériels	*0.75 % capital/an*	2.04
Coûts d'analyse	*15.00 % M.O. opération*	0.04
Sous total		**74.30**
Coûts indirects et généraux		
Salaires	*20 % M.O. maintenance*	0.36
Couts généraux et administratifs	*30 % M.O. total*	0.65
Assurances and taxes	*1.5 % capital/an*	4.08
Royautés	*$Can/t rocks*	0.28
Sous-total		**5.37**
Coûts en Capitaux		
Total des coûts en capitaux	*147 896 241 $Can*	
Période d'amortissement	*20 ans*	
Durée de vie des équipements	*20 ans*	
Financement (intérêts sur le capital)		5.43
Amortissement		13.59
Sous-total		19.02
Total des coûts d'exploitation		**98.70**
Revenus		
Taxe Carbone		
Taux réel de fixation	*235.6 kg CO_2/t roche*	
Capacité de séquestration nette	*356 192 t CO_2/an*	
Revenu de CO_2	20 $Can/t CO_2	
Sous-total		13.09
Vente des carbonates de Magnésium		
Taux de production	680.7 kg/t rocks	
Production annuelle	1 029 282 t MgCO3/year	
Cout unitaire	100 $Can/t MgCO3	
Sous-total		191.61
Vente de magnétite/chromite		8.33
Total des revenus		**213.04**
Profitabilité		**114.34**

Tableau 1.14 Bilan énergétique et impact sur le potentiel de séquestration du procédé

Étape du procédé	**Consommation d'énergie (kWh/trt)**	**Impact sur le potentiel de séquestration (%)**
Transport des résidus	11	1
Broyage	19.508	négligeable
Pompes	1.23	négligeable
Prétraitements thermiques	595	35
Réacteurs de carbonatation	0.048	négligeable
Précipitation	977.960	1
Centrifugeuses	6.79	négligeable

1.4 Conclusions et recommandations

L'étude de la réaction de carbonatation minérale en phase aqueuse de résidus miniers silicatés pour le traitement direct d'un gaz de combustion a permis d'optimiser les paramètres de réaction, d'identifier les mécanismes réactionnels mis en jeu, ainsi que d'évaluer la faisabilité économique d'un tel procédé. Dans un premier temps, il a été démontré que l'utilisation de résidus miniers ne contenant pas de chrysotile, ou encore de brucite, était possible malgré la moins bonne réactivité de ceux-ci. Cela permet d'ouvrir l'applicabilité du procédé développé à un ensemble varié de résidus miniers contenant majoritairement de la serpentine. Bien que la faisabilité de la réaction dans les conditions atmosphériques proches de celles étudiées étaient connues, il a été démontré que les cinétiques lentes étaient accélérées lors du contact avec un gaz de combustion. La carbonatation minérale utilisant des matériaux naturels peut se présenter comme une méthode de séquestration viable. L'élaboration d'un schéma de procédé mettant en jeu des temps de rétention adaptés aux différentes cinétiques associées à la réaction globale a permis d'atteindre des rendements proches de ceux observés dans des conditions de haute température et pression. Par ailleurs, l'accent porté sur l'obtention d'un carbonate de Mg pur offre une importante valeur ajoutée au bilan économique. La vente du carbonate permet en effet de rendre l'implantation d'une usine de traitement industrielle faisable. Peu de technologies proposées pour la séquestration du CO_2 offre un procédé créant un revenu.

Cependant, les résultats obtenus au laboratoire doivent être validés à une échelle pilote. Le traitement d'un gaz réel de combustion doit également être validé, tout en développant le procédé en traitement continu. Un accent tout particulier devrait être porté sur le traitement du gaz en réduisant les conditions de pression (maintenue à 10 bar pour des raisons pratiques). Des essais à pressions réduites ont par ailleurs démontré la faisabilité du traitement sur une batch. De plus, le travail à pression réduite pourra être plus approprié avec un flux continu de gaz. Un effort important doit également être porté à la recherche de méthodologies moins contraignantes pour la réactivation du matériel en cours de traitement. L'efficacité du traitement thermique doit également être poussée à son maximum afin de réduire l'impact de cette étape cruciale du procédé et afin d'obtenir un matériel dont la réactivité est accentuée dès le début du traitement. Par ailleurs, l'évaluation économique doit être affinée afin de s'approcher au plus près de la réalité.

Cette étude n'est que la première pierre dans le développement d'une technologie qui pourrait offrir au Québec, ou à d'autre pays, la possibilité d'allier la pérennité d'industries indispensables au développement du monde de demain sans hypothéquer l'avenir de notre environnement. De plus, la revalorisation de montagnes de résidus comme ceux du sud du Québec apporterait à des régions un nouveau souffle économique ce qui rend l'affaire d'autant plus attrayante.

1.5 Références

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CHAPITRE 2 : ARTICLE 1

Reaction mechanism for the aqueous phase mineral carbonation of heat activated serpentine at low temperature and pressure in flue gas conditions

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RÉSUMÉ

La carbonatation minérale est considérée comme la méthode de séquestration du CO_2 la plus sure d'un point de vue environnemental. Cependant, les cinétiques lentes représentent une contrainte majeure pour l'application de cette réaction au niveau industriel. Jusqu'à présent, aucune étude ne s'est intéressée à la réaction impliquant de la serpentinite avec un gaz ayant une pression partielle de CO_2 relativement faible similaire à un gaz de combustion. Cette étude, s'intéresse à réaction entre une serpentinite finement broyée et activée thermiquement et un gaz contenant 18.2 vol% sous une pression globale modérée. Les effets des conditions expérimentales sur la solubilité du CO_2 et sur la lixiviation du Mg ont été observés. La cinétique de dissolution de la serpentine à également été mesuré afin de déterminer l'étape limitante de cette réaction. Les limitations intervenants à la surface du matériel on été identifiée par spectroscopie électronique à balayage après le traitement de batches successives de gaz par un même solide. Cette étude à démontrée que la réaction de carbonatation de la serpentinite lors du traitement direct d'un gaz de combustion offrait des taux de dissolution accélérée comparativement aux travaux précédents, avec une vitesse de dissolution mesurée de 3.55×10^{-11} $\text{moles.cm}^{-2}.\text{sec}^{-1}$. Cette étude offre une nouvelle perspective pour l'application industrielle d'un procédé de carbonatation minérale pour la réduction des émissions de gaz à effet de serre.

Mots clefs : Carbonatation minérale, Dissolution de la serpentinite, Solubilité du CO2, Mécanismes réactionnels, Traitement des gaz de combustion.

ABSTRACT

Mineral carbonation is known as one of the safest ways to sequester CO_2. Nevertheless, the slow kinetics and low carbonation rates constitute a major barrier for any possible industrial application. To date, no studies have focused on reacting serpentinite with a relatively low partial pressure of CO_2 (pCO_2) close to flue gas conditions. In this work, finely ground and heat-treated serpentinite [$Mg_3SiO_2(OH)_4$] extracted from mining residues was reacted with a 18.2 vol.% CO_2 gas stream at moderate global pressures in order to investigate the effect on CO_2 solubility and Mg leaching. Serpentinite dissolution rates were also measured in order to define the rate limiting step. Successive batches of gas were contacted with the same serpentinite to identify surface limiting factors by using SEM analysis. Investigation of the serpentinite carbonation reaction mechanisms under conditions close to a direct flue gas treatment showed that increased dissolution rates could be achieved relative to prior work, with an average Mg dissolution rate of 3.55×10^{-11} moles.cm^{-2}.sec^{-1}. This study provides another perspective of the feasibility of applying a mineral carbonation process to reduce industrial greenhouse gases (GHG) emissions from large emission sources.

Keywords : Mineral carbonation, Serpentinite dissolution, CO_2 solubility, Reaction mechanisms, Flue gas treatment

1. Introduction

Increasing greenhouse gases (GHG) and more particularly CO_2 emissions is recognized to impact on climate change.[1] Research has focused on different mitigation solutions, [2] including Carbon Capture and Storage (CCS). Capture and sequestration techniques may involve gas-liquid, gas-solid and solid-liquid reactions including, adsorption, absorption processes.[3] Geological sequestration, for example, requires an understanding of the interactions between a supercritical CO_2 fluid and the geological formation in order to predict mineralization of the reservoir and thus the CO_2 behavior once injected in the ground. [4-6] Mineralization of CO_2 by mineral carbonation is considered as one of the safest and the most sustainable way to sequester CO_2. [7-11] Such a phenomenon occurs naturally and involves the reaction between a fluid containing dissolved CO_2 with alkaline minerals to form carbonates.[12, 13] Research on mineral carbonation has focused to date on reacting the most abundant alkaline minerals such as olivine $[(Mg,Fe)_2SiO_4]$, serpentinite $[(Mg,Fe)_3Si_2O_5(OH)_4]$ and alkaline wastes such as cement or steel slag.[14-16] Most of the experiments with these materials tend to react a concentrated CO_2 gas under dry or aqueous conditions.[17, 18] Further, high temperatures and pressures are generally applied in order to increase the reaction kinetics.[11, 17, 19-22] Such conditions induce high energy costs and stray far from the reality of post combustion flue gas conditions, making them less industrially feasible.[14, 23] More recent research has focused on lower temperature and pressure conditions, mostly to explain and understand naturally occurring processes.[24-29]

In order to implement mineral carbonation into an industrial process, the mechanisms, thermodynamics and kinetics of the relevant reactions must be understood. Studies at higher temperatures and pressures have generally used a thermodynamic approach in order to optimize conditions.[8, 12, 30-32] These papers report that reaction is generally controlled by surface processes following a shrinking core model and that the surface area of the reacting particles is the limiting factor.[21, 33] For reaction occurring under atmospheric conditions, such as those observed with mining residues, similar processes have identified other limiting factors including surface wetting and CO_2 partial pressure.[34-37]

To date, very few studies have considered the possibility of direct flue gas carbonation of mineral residues within an aqueous phase for CO_2 sequestration. Such operation requires changes to the process scenarios considered previously. [38, 39] A major change is to create a two-step process that separates the CO_2 capture step from the precipitation of carbonates. The first step is mostly controlled by CO_2 solubility, influenced by temperature and the partial pressure of CO_2 (pCO_2).[40-44] In the case of a cement plant, this CO_2 content can vary from 15 to 25 vol % depending upon the type of raw material used in the kiln and of the type of fuel used. At lower pCO_2 it is necessary to operate at lower temperatures in order to maintain a good CO_2 solubility in accordance with Henry's law.[43] In addition, operation at flue gas pressures close to atmospheric avoids expensive gas compression which would otherwise impact on the global process cost. Such changes in the operating conditions require further work in order to understand the factors that will limit reaction and to correctly optimise these reaction parameters. Recent work reported that even at lower pCO_2, the global dissolution rate of brucite could be accelerated due to the presence of ligands such as HCO_3^-.[45] The identification of similar processes when reacting serpentinite would lead to a re-consideration of the potential of using such material as a CO2 sequestration media.

This paper explores the effects of low temperature and low pressure conditions on mineral carbonation reaction pathways. Experiments are performed by contacting a heat-treated serpentinite extracted from mining wastes with a gas of composition close to that of a cement plant flue gas (18.2% CO_2, 4% O_2 balanced with N_2). The effects on the CO_2 solubility and the serpentinite dissolution rate are measured. Finally, a microstructural analysis highlights the limiting processes in serpentinite dissolution.

2. Material and methods

2.1 Sample preparation, characterization and analytical methods

Residues were sampled from southern Québec, near Thetford Mines, at the old American Chrome, chromite mining site in Coleraine. Residues were extracted from surrounding rocks and thus presented a heterogeneous size. The chemical composition of the raw solid feedstock is presented in Table 1. Prior to reaction, the sample was crushed using a jaw crusher and ground by an impact disc mill (*Bleuler-Mill*, NAEF) in order to obtain a median grain size of 28.4 ± 1.8 µm. The surface area was measured using nitrogen BET adsorption and was found to be 21.6 m^2/g. X ray diffraction analysis of the sample identified three major crystalline phases, lizardite, magnetite and chromite.[46] Heat activation of the sample was conducted in a muffle furnace (*Furnatrol 133*, Thermolyne Sybron Corporation) at 650°C for 30 min.[30] Chemical analyses of liquid and solid samples used Induced Chromatography Plasma-Atomic Emission Spectra (ICP) analysis (*Vista AX CCO Simultaneous ICP-AES*, Palo Alto, CA, USA). Solid samples were fused using metaborate lithium prior to ICP analysis (*Corporation Scientifique Claisse*, Québec Canada). Inorganic carbon analyses were completed with a TOC-V CPH (*Shimadzu*, Tokyo, Japan) on liquid samples. Crystalline phases were identified by X-Ray diffraction (X-RD) analysis performed at Laval University (*Siemens D5000* diffractometer). Scans were taken for 2θ ranging from 5 to 65° with steps of 0.02°/s, with a Cu anode. Scanning Electron Microscopy (SEM) was performed on a Zeiss Evo 50 coupled with an Energy Dispersive X-Ray Spectrometry (EDS) analyzer for semi quantitative sample analysis. Specific area of the sample was determined using the Brunauer-Emmett-Teller (BET) theory with a BEL SORP-Max analyzer (Bel INC, Japan). N_2 sorption and desorption isotherm were realized at 77°K followed by a overnight degasing step at 423°K under a pressure below 10^{-5} torr. Analyzis gave a specific surface area of 21.6 $m^2 . g^{-1}$.

2.2 Reaction apparatus and experimental conditions

All the reactions were completed in a 300 mL stirred reactor *Model 4561* (*Parr Instrument Company,*Moline, IL, USA). During experiments, temperature, pressure and agitation were controlled and recorded using a 4848 modular Controller (*Parr Instrument Company*). The feed gas mixture had a certified composition of 4 vol.% O_2, 18.2 vol.% CO_2 balanced with N_2 (*Linde,* Canada). The reaction conditions used were optimized in our prior work, as a pulp density of 15 wt.% (150 g/litre) within a volume of water of 75 mL, giving an initial solids charge of 11.25g and gas phase volume of 225 mL.[46] The heat treated serpentinite was mixed with water and the pH measured before closing the vessel. The agitation was set at 600 rpm and then the gas injected. The exit gas valve was close after 10 ± 5 seconds, allowing the air contained in the reactor to be purged. Once the desired global pressure was reached all the valves were closed. Global pressure decreased between 0.2 to 2.2 bar, depending upon the amount of gas initially injected, due to CO_2 absorption into the solution. After reaction, a gas sample was collected into a sampling bag and the CO_2 content measured using an infra-red CO_2 analyzer (*Model 906, Quantek Instrument,* MA, USA). The pH of the final pulp was measured and the pulp filtered to separate the liquid and the solid fractions.

2.3 Mathematical Simulations

The reaction of serpentinite with carbon dioxide in an aqueous phase was modelled using PHREEQC 3.0.6-7757 software. Equilibrium constants and reaction enthalpy were calculated using HSC Chemistry 7.0.

3. Results and discussion

3.1 Impact of heat-treated serpentinite on CO_2 solubility

Experiments were initially conducted to measure the effect of the heat-treated serpentinite at low pressure and ambient temperature on the CO_2 uptake. The amount of CO_2 lost in the gas phase measured after 15 minutes of reaction is plotted against the initial partial pressure of CO_2 in Figure 1. In order to provide a comparison, the CO_2 loss at equilibrium were also modeled using PHREEQC software for the dissolution of CO_2 both in pure water and in a solution of lizardite. The same gas composition, volume of liquid and amount of solid feedstock as those used in the lab were utilized for these simulations. The initial pH of the solution was set at 10.5 as observed during the laboratory tests. Lizardite was chosen for the feedstock as it corresponds to the major phase of the serpentinite used for the lab tests. The equilibrium constant and enthalpy for the dissolution of lizardite (Eq 1) was calculated using HSC Chemistry 7.0 software, giving $\log K = 34.646$ and $\Delta H_{298K} = -255.3$ KJ. The formation enthalpy and entropy were taken from Holland and Powell [47] and integrated into the HSC database.

$$Mg_3Si_2O_5(OH)_4 + 6H^+ = 3Mg^{2+} + 2H_4SiO_4 + H_2O \quad (1)$$

The experimental concentrations of CO_2 in the liquid phase at a temperature of 22 ± 3°C were in accordance with model predictions in the presence of lizardite at 20°C and 25°C. Increased CO_2 loss for simulations with lizardite relative to pure water showed that CO_2 solubility is favoured in the presence of the solid feedstock (Figure 1). The generation of dissolved Mg^{2+} in the solution through Equation 1 facilitates the formation of $MgHCO_3^+$ complexes, which reduces solution saturation of carbon dioxide. CO_2 solubility is thus increased compared to conditions with water only.

The presence of $MgHCO_3^+$ also impacts the pH of the solution. Initially, directly after solid addition, the pH of the solution was around 10.5 but this falls to between 7.5 and 8.5 after the reaction period. The same pH range was reported for the simulations with lizardite where the pH at equilibrium was predicted to be between 6 and 8. Conversely, pH values for simulations without solids varied between 3.6 and 4.3. Acidification of the solution induced by CO_2 dissolution was clearly buffered by the presence of dissolved species when solids were present. Such buffer effects also allowed more CO_2 to be dissolved in respect to the carbonate equilibria (Eq 2 - 3).[42]

$$CO_{2(g)} \leftrightharpoons CO_{2(l)} \tag{2}$$

$$\mathrm{CO_{2(l)} + H_2O \leftrightharpoons HCO_3^- + H^+} \leftrightharpoons CO_3^{2-} + 2H^+ \tag{3}$$

For reaction at 25°C and 10.5 bars total pressure, simulations showed that at equilibrium, the carbon within the liquid phase was distributed with 90% as HCO_3^-, 7% as $CO_{2(aq)}$, 1.9% and $MgHCO_3^+$. The amount of aqueous $MgCO_3^{2-}$ and CO_2^{3-} was insignificant. The model also showed that precipitation of solid carbonates under the form of magnesite [$MgCO_3$] with total amount of 1.709×10^{-2} moles and which represents 98% of the carbon initially lost from the gas phase. Nevertheless, it is important to keep in mind that modeled value describes the system at equilibrium. On the contrary experimental results showed that 85 ± 2 % of the carbon lost from the gas phase was in the liquid phase after 15 minutes reaction. It clearly indicates that the carbonates precipitation kinetic is much slower compared with CO_2 dissolution in water. Thus the low quantity of $MgHCO_3^+$ described by the model does not correspond to experimental observations were the system is far from equilibrium. In addition, in the present temperature conditions hydrated carbonates such as nesquehonite ($MgCO_3.3H_2O$) or hydromagnesite ($MgCO_3.5H_2O$) would be observed before magnesite.[48]

3.2 CO_2 dissociation as a Mg leaching promoter

Dissolution of a mineral solid is known to follow two distinct kinetic regimes; a first rapid reaction between surface sites and reactants, mostly protons, hydroxide ions or ligands such as HCO_3^- resulting in the formation of surface species, followed by a slower phase were the metal is detached from the surface and goes into solution.[42] In the case of silicate minerals, rapid mass transfer is initially observed due to proton exchange with available cations on the mineral surface.[49] The rapid increase in pH observed after adding the serpentinite into solution reflects such a phenomenon. Further, thermal activation of the serpentinite is known to increase the efficiency of Mg leaching under acidic conditions.[50, 51] Such observation was also made in our case (even before CO_2 addition) as the initial pH varied from 10 for raw serpentinite to 10.5 after heat treatment. When the gas is added, CO_2 dissociation generates protons and HCO_3^- ions in solution, which further enhance the formation of surface species.

Such mechanisms were confirmed by plotting the concentration of Mg against the Dissolved Inorganic Carbon (DIC) in solution after reaction (Figure 2), for a range of experiments at different initial pCO_2. As discussed above, an increased partial pressure of CO_2 increased the concentration of inorganic carbon dissolved in solution. The linear relationship observed highlights the relationship between the Mg leached from the solid and the DIC resulting from CO_2 dissolution. The value for the slope coefficient is almost equal to one, implying that the two concentrations are linked. The modeling discussed above showed the presence of magnesium bicarbonate in solution with a predominance of bicarbonate ion. In the experimental conditions, it could be stated that most of the Mg present in solution would be under the form of $MgHCO_3^+$ as such a complex is a precursor for magnesium carbonate formation.[48, 52]

3.3 Mg dissolution rates

Results discussed to date have confirmed that reaction between heat-treated serpentinite and a low CO_2 partial pressure gas at ambient temperature is strongly correlated with the Mg leached from the solid. Figure 3 presents the kinetics of Mg leaching for the reaction with a global pressure of 10.5 bars (pCO_2 = 1.91 bars). As previously discussed, silicate dissolution follows two kinetic steps. There is an initial very rapid dissolution due to proton exchange with available cations on the mineral surface. This is followed by a period of slower kinetics.[53, 54] A similar pattern was observed under our conditions. After the initial very rapid reaction period, the concentration of dissolved Mg followed a parabolic relationship with respect to time. This relationship reflects dissolution controlled by the transport of the dissolved species from the surface to the bulk solution.[42] The data was fitted to a parabolic rate law as given by Eq 4:

$$C_{Mg} = kt^{1/2} + C_{Mg_0} \tag{4}$$

With, C_{Mg} the concentration of dissolved Mg (moles.cm^{-2}), *k* the rate constant (moles.cm^{-2}.sec^{-1}) and $C_{Mg_0}$the concentration of Mg at t = 0 (moles.cm^{-2}). Regression analysis gave a rate constant of 3.98×10^{-11} mol.cm^{-2}.sec$^{-1/2}$ and a C_{Mg_0} equal to 1.61×10^{-9} moles.cm^{-2} giving a R^2 of 85% (Eq 5). The global rate measured was;

$$C_{Mg} = 3.98 \times 10^{-11}x + 1.61 \times 10^{-9} \tag{5}$$

These model equation parameters are in the same range as those presented in the literature for lizardite dissolution for a pH between 7 and 10 without application of CO_2 .[53]

The average Mg dissolution rate was 3.55×10^{-11} moles.cm^{-2}.sec^{-1} which fits between the rates reported for brucite dissolution under 10% and 50% CO_2 atmospheres.[45] On the other hand, the rate was higher than the value of 1×10^{-13} mol.cm^{-2}.sec^{-1} reported for chrysotile dissolution at 25°C in a pH range of 7-10.[55] . This difference can be linked to both the effect of the CO_2 dissolution and the heat activation of the serpentinite. As well, the average particle size used in the present study was significantly smaller which impacts on the surface area of the sample and thus promotes serpentinite dissolution.

In addition to validate the effect of the pCO_2 on the serpentinite dissolution, the initial Mg dissolution rates (15 min assays) were calculated as follows (Eq 6):

$$r = \frac{1}{SA_{iserp}} \frac{\partial C_{Mg}}{\partial t} \approx \frac{1}{SA_{iserp}} \frac{(C_{Mg}-0)}{t} \tag{6}$$

Where, C_{Mg}stands for the moles of Mg in solution at time *t*, SA_{iserp} is the total initial surface area of serpentinite and t is the time of contact between the gas and the pulp (seconds). The relationship between this initial rate and pCO_2 is linear for pCO_2 less than or equal to 4 bar (Figure 4), confirming the stoichiometry of Equations 1-3 (that is, one mole of CO_2, generates $2H^+$, which in turn generates one Mg^{2+}).

Nevertheless, increasing the *pCO_2* beyond 4 Bar tends to result in solution saturation, as evidenced by the lower initial rate at 8Bar in Figure 4. While serpentinite dissolution was favoured under our conditions, carbonate precipitation will follow a slower kinetic rate. Saturation will thus eventually limit CO_2 uptake. Such an issue could be overcome by occasionally refreshing the solution to prevent saturation. In addition, carbonates could be precipitated under more favorable conditions in a separate downstream step, without impacting on the flue gas contacting step. The advantage of this approach is that it allows production of a pure carbonate product, separated from the serpentinite matrix, giving a potential by-product sale. In addition, the leaching tests were run under batch wise conditions. It is thus possible that reaction was also limited by CO_2 diffusion from the gas liquid interface too. Under continuous gas flow reaction rates may have been increased.

While most studies have focussed on increasing serpentinite dissolution using strong acids such as HCl or H_2SO_4, or by adding organic salts such as citrates [56, 57], the serpentinite dissolution in the presence of carbonic acid as a weak acid presented here appears competitive. In addition, as for this other work, the limiting step was identified to be the surface product diffusion from the surface to the bulk solution.

3.4 SEM analysis

In addition to the issue of solution saturation described above, other authors have observed the formation of a passivation layer under high temperature and pressure conditions.[19, 58] Mining residue weathering under atmospheric conditions is also known to be affected by passivation, with a Si-rich layer forming on the surface of the material, which limit the CO_2 diffusion through to the Mg oxides.[35]

In the present work, successive batches of gas at a global pressure of 10.5 bars each were contacted with the same solid feedstock. Such conditions allowed us to increase the amount of CO_2 introduced in the vessel without operating at high pressure. Observations showed that the efficiency of the CO_2 treatment decreased batch after batch. Such a decrease could be due to solution saturation and/or because of surface passivation. In order to reduce the impact of the solution saturation, the liquid was replaced after each two batches of gas. While CO_2 uptake was maintained, no more Mg was leached from the solid after six batches of gas treated (three batches of liquid). Different techniques were tried in order to re-activate the solid feedstock. Among them, another grinding cycle followed by another heat treatment gave the best results.[46] Equivalent CO_2 removal efficiencies as observed with a fresh solid were achieved when this re-activation was used. Six more batches were contacted for a total of 12 batches of gas treated by the same solid feedstock. Nevertheless, no greater efficiency in either Mg leaching or CO_2 removal were observed when contacting more batches of gas even with another activation.

Polished sections were made with the powder recovered after being contacted for 12 batches of gas in order to understand the type of surface limitation occurring. SEM backscatter analysis revealed the presence of two different types of morphology; Larger grains showing a less dense layer at the surface (Figure 4a), and agglomerations of particles smaller than 25 μm (Figure 4b). The presence of a layer having a smaller mass was observed mostly on larger grains (point A2 and A3). EDS analysis showed a composition difference between the core of the grain (point A1) and the surface layer (point A2), illustrating the surface process occurring on the grains. The amount of silica and magnesium were respectively higher and lower on the surface compared to the core analysis. However, the surface layer cannot be readily attributed to any particular form of magnesium carbonate. The Mg:O ratios did not correspond to any particular carbonate likely to form such as nesquehonite, dypingite or hydromagnesite and hence was probably a complex mixture of many minerals.[48] The amount of Mg was clearly lower than the surrounding phase, while silica and oxygen concentrations stayed the same. Composition analysis confirmed that the reaction is following a shrinking core model with an accumulation of ash layer constituted of non-reactive materials on the surface of the grains.[59] Most of the surfaces showed an ordered structure. Nevertheless, the point A3 on Figure 4a shows what looks like a disordered ash layer. Smaller, translucent particles within the cluster of dark mass showed a lower Mg concentration compared with the ordered layer observed on other grains (point A2). This might be explained in two ways. Firstly, the ash may be agglomerated on the bigger grain with other smaller non-reacted particles. Alternatively, the Mg depleted area is the result of the larger grain reaction.

A significant concentration of agglomerates of smaller particles was also observed within the section (Figure 4b). A similar Mg ratio was measured within the darker particles here (point B2 and B3) to that observed in Figure 4a. Such very fine particles could represent the non-reactive material removed from the grain surface by the grinding cycle and the heat treatment applied after the 6th batch of gas. While some of the particles (point B1) presented a similar layer as those observed on the larger ones, such agglomeration can represents an important limitation for the reaction, as non-reacted particles are also present here. In addition, several grains of magnetite (Fe_3O_4) are present on both pictures (white particles). Large grains presented small white dots within the core of the particles, showing small magnetite inclusions within the serpentinite. In addition, such inclusions can potentially limit dissolution. [34]

3.5 Serpentinite as direct CO_2 flue gas sequestration media

This study highlights the potential of serpentinite as a medium to directly sequester CO_2 from a cement plant type flue gas. Similar limitations as observed under other conditions were identified. Nevertheless, the serpentinite dissolution showed accelerated rates, under ambient temperature and moderate CO_2 partial pressure, compared to other reported data in such conditions.

Further experiments were conducted to confirm whether the liquor obtained from each experiment could be used to generate solid magnesium carbonate. In this case, solutions obtained from the contact of two batches of gas were removed from the reaction vessel and placed in a stirred jar and held at 40°C. Results showed that 63 wt% of the Mg was precipitated within three hours, with 95wt% of the Mg transformed into solid carbonates within 18 hours. However, such high final yield was partially attributed to solution evaporation over an extended period while such phenomenon was insignificant after three hours precipitation. XR-D analysis of the precipitated solids indicated only a single crystal phase, Nesquehonite [$MgCO_3$ $3H_2O$] (Figure 5). In addition, EDS analysis of the SEM images confirmed that the element ratios were in accordance with those of the Nesquehonite (Figure 5). Morphological information given by the secondary electron SEM image also corresponded to observations described in the literature.[60] The important point here is the purity of the precipitated carbonate. Such a by-product can present an important sale value and thus overcome the processing costs, already reduced by the low temperature and pressure conditions.

While experimental conditions require further optimization, the promising observations made here open new possibilities into the application of mineral carbonation to reduce industrial CO_2 emissions. By assuming that a carbonation efficiency of 50% (t CO_2 sequestered/t of serpentine required) can be reached, a total of 0.378 Mt CO_2 per year could be sequestered by a plant with a capacity of 200t of serpentine/hour using this approach, which represents almost a half of the Québec's cement/lime industries annual emissions.[61] Southern Québec province has large quantities of mafic mining wastes (2 Gt) within 200 km distance from important industrial areas.[62] As restrictive measures to reduce GHG emissions form the industrial sector are implemented, such sequestration potential should be considered as a priority.[63, 64]

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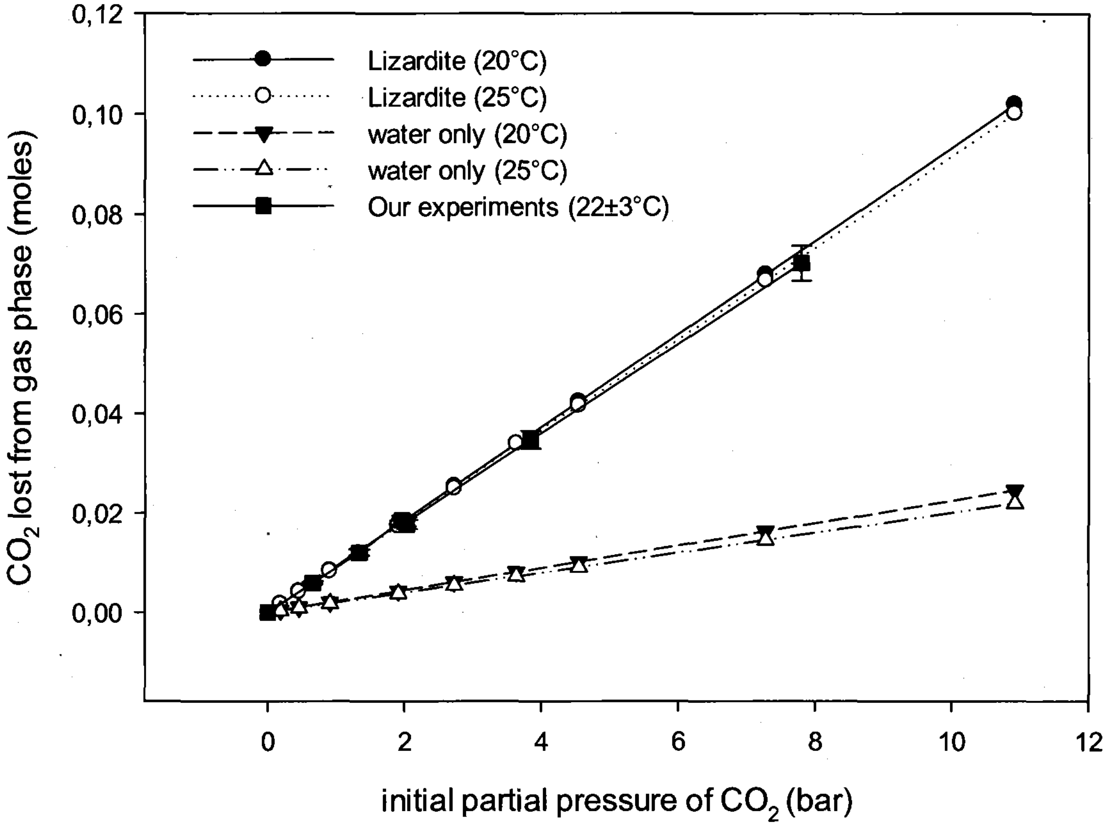


Fig. 1 : Comparison of the experimental lost of CO_2 from the gas phase measured after 15 minutes reaction with 150 mg/L heat treated serpentine with values modeled with PHREEQC for the same conditions with pure lizardite (log K= 35.41) and water only at 20°C and 25°C. Errors bars stand for 5% error

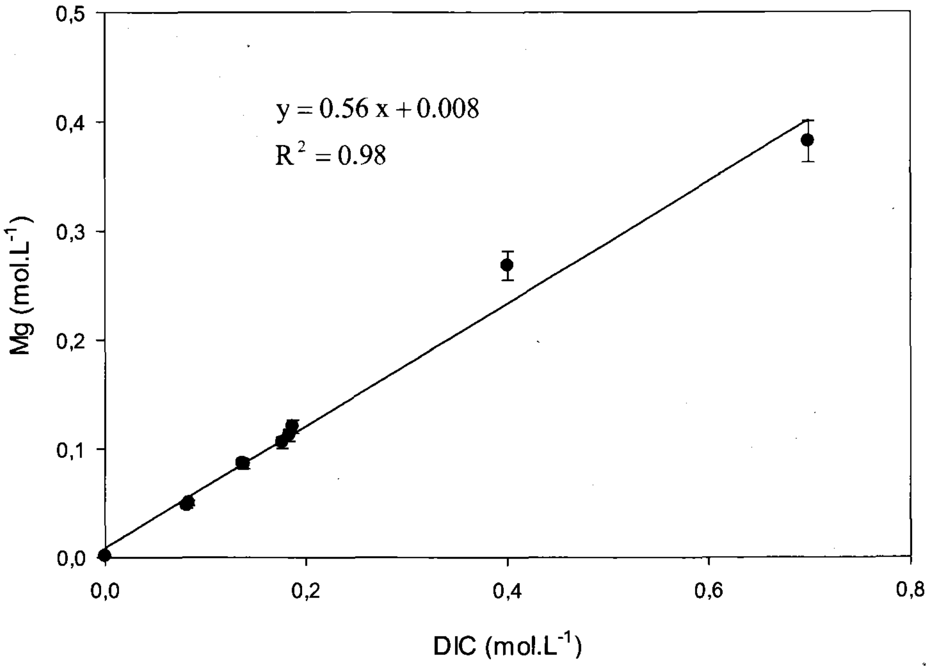


Fig. 2 : **Concentration of Mg against concentration of dissolved inorganic carbon (DIC) in solution after 15 min of reaction with 150 g/L solid concentration at ambient temperature for different pressures. Error bars stands for 5% error.**

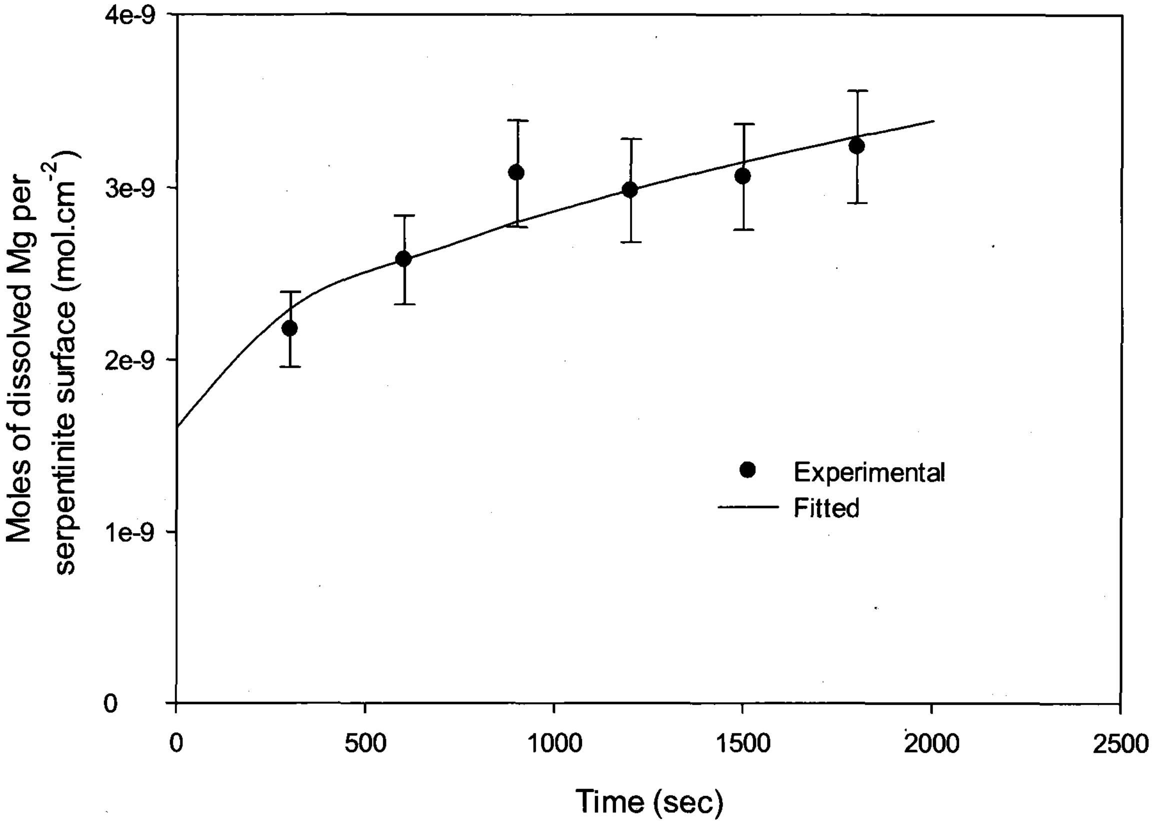


Fig. 3 : Dissolved Mg concentration in solution kinetic. Errors bars stands for 10% error.

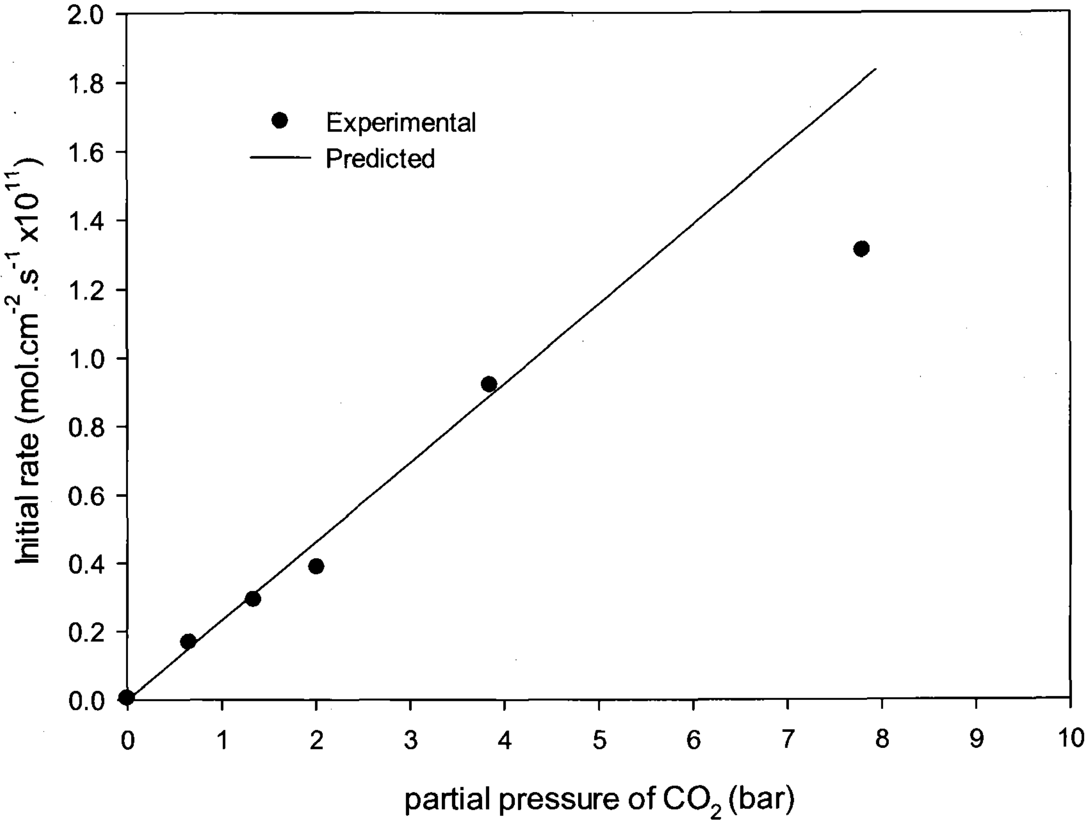
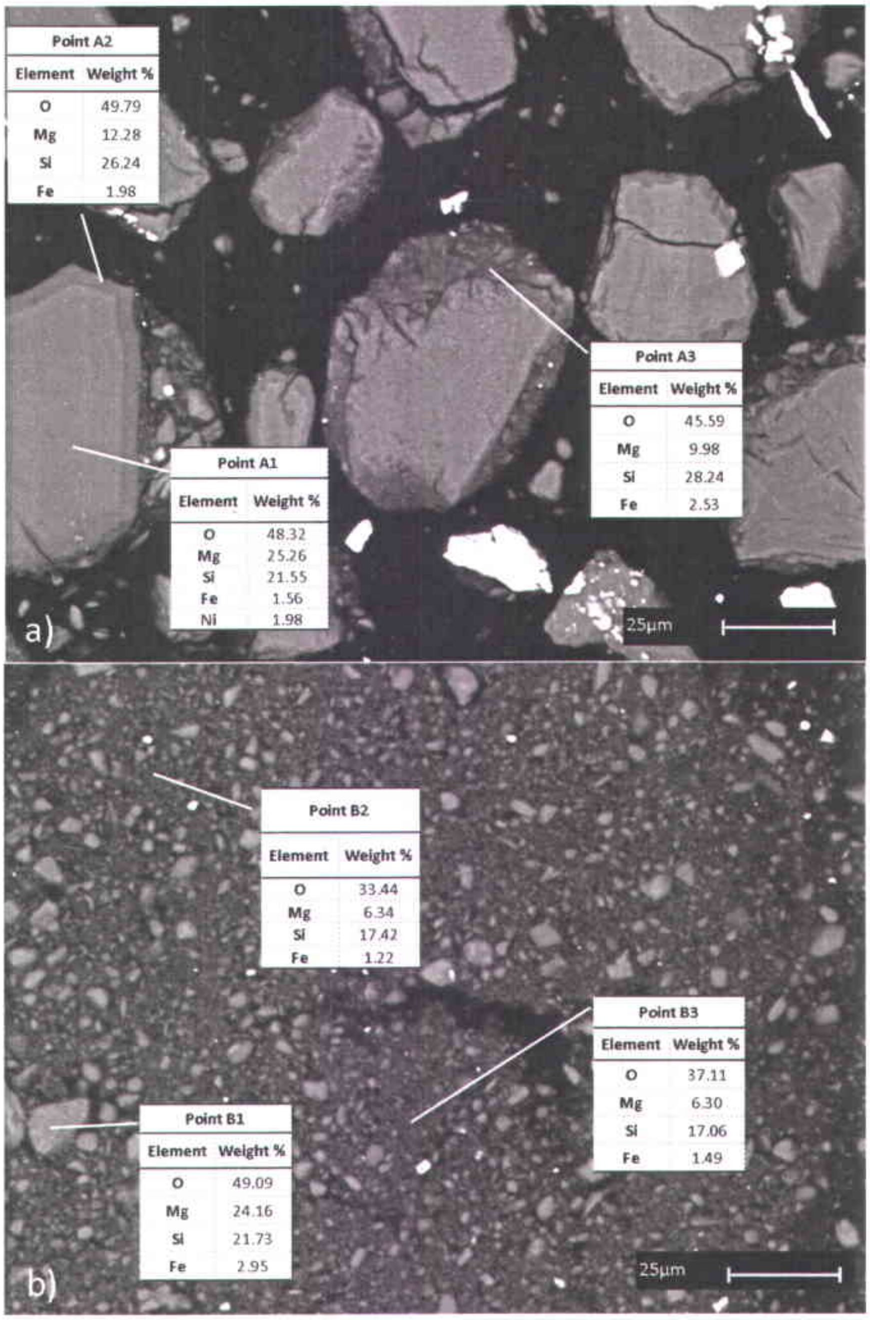


Fig. 4 : Initial dissolution rate as function of the partial pressure of CO_2



Point A2	
Element	Weight %
O	49.79
Mg	12.28
Si	26.24
Fe	1.98

Point A3	
Element	Weight %
O	45.59
Mg	9.98
Si	28.24
Fe	2.53

Point A1	
Element	Weight %
O	48.32
Mg	25.26
Si	21.55
Fe	1.56
Ni	1.98

Point B2	
Element	Weight %
O	33.44
Mg	6.34
Si	17.42
Fe	1.22

Point B3	
Element	Weight %
O	37.11
Mg	6.30
Si	17.06
Fe	1.49

Point B1	
Element	Weight %
O	49.09
Mg	24.16
Si	21.73
Fe	2.95

Fig. 5 : SEM pictures (x 2000) and EDS analysis of two different areas within a polished section of serpentinite after reaction with several batch of gas. a) presents larger grains showing composition variations at the surface, and b) agglomerations of smaller grains with identical compositions variations as observed on the larger grains.

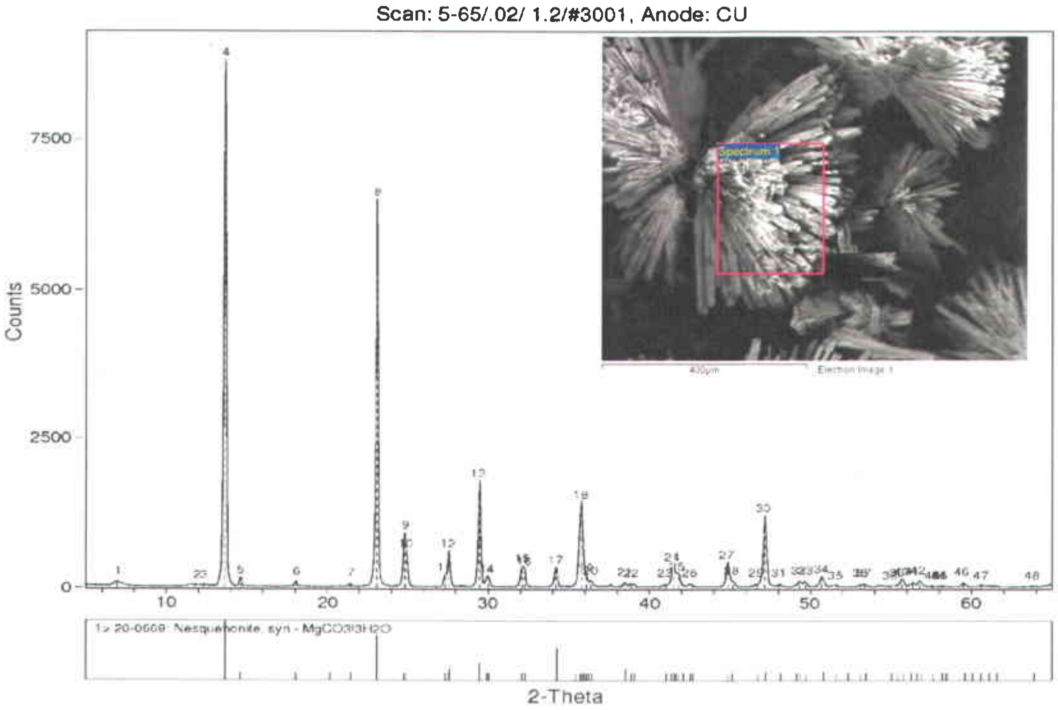


Fig. 6 : XR-D and SEM picture of Mg carbonates precipitated from the solution obtained after successive batch of gas treated.

Table 1

Chemical composition of the raw solid feedstock. Only major elements are presented.

Elements	Units	Values
Al_2O_3	wt%	1.6
CaO	wt%	0.04
Cr_2O_3	wt%	0.9
Fe_2O_3	wt%	19
MgO	wt%	47
MnO	wt%	0.05
SiO_2	wt%	42
C_{inorg}	wt%	0.24
LOI [a]	wt%	11.6

[a] Lost on ignition.

CHAPITRE 3 : ARTICLE 2

Parameters optimisation for direct flue gas CO_2 capture and sequestration by aqueous mineral carbonation using activated serpentinite based mining residue.

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RÉSUMÉ

La réaction naturelle de carbonatation minérale est connue pour être une des solutions permettant de réduire de façon significative les émissions de gaz à effet de serre. L'intégration de ce processus pour la séquestration des émissions de CO_2 émis par les grandes industries n'a cependant pas réussi à démontrer son efficacité tant chimique qu'économique. À ce jour, la recherche s'est essentiellement concentrée sur le traitement d'un gaz concentré en CO_2 avec des roches alcalines. Des taux de carbonatation prometteurs ont été atteins mais la nécessité d'opérer dans des conditions de température et de pression élevées limite la faisabilité de l'application des procédés développés. Cet article décrit l'optimisation des paramètres opératoires pour le traitement direct d'un gaz de combustion par carbonatation minérale, en utilisant des résidus miniers majoritairement constitués de serpentine, finement broyés et activé thermiquement. Le gaz est ainsi mis en contact avec une pulpe contenant les résidus à température ambiante et à pression modérée (10.5 bar). Une fois la solution saturée en CO_2 et en Mg dissout, celle-ci est filtrée et les carbonates précipités dans une deuxième étape. Le solide est quand-t-a lui de nouveaux mélangé avec de l'eau pour traiter plus de gaz jusqu'à ce que le taux de Mg dissout soit nul. Les paramètres réactionnels tels que la densité de pulpe, le ratio du volume de gaz sur le volume de liquide, le temps de réaction et la taille des particules ont étés étudiés pour le traitement en batch d'un gaz contenant 18.2 vol.% de CO_2. Par la suite le scenario de recirculation des phases liquides et solides à été développé en réalisant le traitement de batch successives de gaz. Cette approche innovatrice à permis d'obtenir des rendements de traitement du CO_2 contenu dans le gaz de l'ordre de 62.5 m.% et de dissoudre 64 m.% du Mg contenu dans le résidu, pour atteindre un rendement de carbonatation de 0.55 kg CO2 traité pour 1 kg de résidu. De plus l'utilisation de conditions de température et de pression plus douces, ajouté au potentiel de revente du carbonate de magnésium quasi pur rendent l'application industrielle d'un tel procédé plus réaliste.

Mots Clefs : Capture du CO_2, carbonatation minérale, résidus miniers alcalins, carbonates de magnésium, traitement direct d'un gaz de combustion.

ABSTRACT

Naturally occurring mineral carbonation can significantly reduce GHG emissions. Adapting the reaction in order to sequester post combustion CO_2 has been seen as a potential industrial mitigation pathway, but such a process must be chemically and economically efficient. Research has focused to date on reacting a concentrated CO_2 stream with alkaline rocks. Significant carbonation rates where reached but required a system operating at high pressure and temperature. This article describes the parameters optimization for direct flue gas CO_2 capture and sequestration when using finely ground heat activated serpentine derived from mining residues. The gas is contacted with the minerals in an aqueous phase at ambient temperature and moderate pressure (10.5 Bar). Once the solution is saturated with dissolved CO_2 and magnesium, it is filtered and carbonates precipitated in a downstream operation. The solid is mixed with fresh water and recirculated to treat more gas until no further magnesium can be leached from the solid media. Reaction parameters such as the pulp density, the volumetric ratio of gas to liquid, the reaction time and the particle size were investigated with a 18.2% CO_2 gas stream in a batch mode. This innovative approach permits the use of moderate temperature and pressure conditions and the production of pure magnesium carbonates with a potential sale value. After parameter optimisation, batch mode tests showed that 64 wt% of the magnesium could be leached from the solid and that 62.5 wt% of the CO_2 removed from the gas phase giving a ratio of 0.55 kg of CO_2 sequestered per kg of residues.

Keywords : CO_2 capture, mineral carbonation, alkaline mining residues, magnesium carbonate, direct flue gas treatment.

1. Introduction

Mineralization of carbon dioxide is part of the well-known natural silicate weathering process. Carbonic acid, resulting from the dissolution of CO_2 in rain water, reacts with an alkaline mineral to form carbonates (Huijgen, 2003; Lackner, 2002). The use of mineral carbonation as a CO_2 emissions mitigation route was first mentioned by Seifritz (1990). The advantages of such an approach over other carbon capture utilisation and storage (CCUS) techniques are that carbonates are stable, environmentally benign and can potentially be sold for profit (Gerdemann et al., 2003; Maroto-Valer et al., 2005). Mineral carbonation reactions are exothermic and spontaneous (IPCC, 2005), even though the natural reaction kinetics can be slow. Alkaline earth metal carbonates such as calcium and magnesium (the most abundant elements) are generally used for mineral carbonation. They are usually found in nature within a silicate crystalline matrix such as wollastonite, olivine and serpentine. The associated reactions are presented below;

$$CaO + CO_2 \rightarrow CaCO_3 \tag{1}$$

$$MgO + CO_2 \rightarrow MgCO_3 \tag{2}$$

$$CaSiO_3\,(wollastonite) + CO_2 \rightarrow CaCO_3 + SiO_2 \tag{3}$$

$$Mg_2SiO_4\,(olivine) + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 \tag{4}$$

$$Mg_3Si_2O_5(OH)_4\,(serpentine) + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \tag{5}$$

Direct carbonation is by far the most interesting CCUS route as the reaction takes place in one step. The simplest reaction is to directly contact the alkaline metal bearing minerals with the CO_2 containing gas phase. Nevertheless, such reaction conditions need preconditioning of the minerals in order to operate at acceptable temperature and pressure conditions (Bearat et al., 2002; Butt et al., 1997; Zevenhoven and Kavaliauskaite, 2004). On the other hand, reaction under aqueous conditions can be a more feasible route, as metal ions are dissolved from the solid media at the same time, as CO_2 forms carbonic acid when it dissolves into water (IPCC, 2005). For example,

$$CO_{2(g)} \leftrightharpoons CO_{2(l)} \tag{6}$$

$$CO_{2(l)} + H_2O \leftrightharpoons HCO_3^- + H^+ \leftrightharpoons CO_3^{2-} + 2H^+ \tag{7}$$

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2Si(OH)_4 + H_2O \tag{8}$$

and

$$Mg_3Si_2O_7 + H^+ + H_2O \rightarrow 3Mg^{2+} + 2Si(OH)_4 \tag{9}$$

Previous studies have focused on reaction with a pure CO_2 gas stream. The most relevant carbonation rates in such conditions were obtained by Gerdemann et al. (2007), where 73.5% of a previously heat treated serpentine was carbonated under 115 atm at 155°C with a 0.64 M $NaHCO_3$ and 1 M NaCl carrier solution for 1 h. A multiple step process using pH swing, where magnesium was leached in an acidic mixture prior to carbonation, showed 65% carbonate conversion (Park and Fan, 2004). However, working with a gas concentrated in CO_2 necessitates an expensive preliminary capture phase. The additional energy inputs required for the preparation of the ore prior to carbonation, added with the requirements of 55 000 tons of rocks per day to sequester the CO_2 generated by a 1GW coal fired power station, led a US research team to conclude that industrial application was not feasible (Gerdemann et al., 2007; O'Connor et al., 2005). However, very few studies describe the use of mineral carbonation with untreated flue gas streams and natural minerals. Such operation would significantly reduce the global cost. One exception is the work by Werner et al. (2013) who studied heat treated serpentine carbonation at low temperature and pressure in flue gas conditions. They stated that reaction was limited by solution equilibrium which limited serpentine dissolution. The maximum carbonation efficiency achieved was 20% conversion.

In addition, in order to reduce processing costs, research has also turned towards other mineral sources such as magnesium and calcium concentrated alkaline wastes. Among them, ultramafic mining residues offer a good alternative (Goff and Lackner, 1998). A range of mining residues can be used such as those from chrysotile, diamond, nickel and chromite mining operations. More generally, tailings containing abundant magnesium-silicates and low acid generating sulfide minerals are suitable (Wilson et al., 2009). Naturally occurring carbonation of such tailings is known (Huot et al., 2003; Pronost et al., 2011; Wilson et al., 2009). Wilson et al. (2009) reported passive carbonation of more than 10 year old tailings in Western Canada, where an accelerated weathering process led to 0.3% carbonation with the formation of nesquehonite ($MgCO_3$, $3H_2O$), dypingite [$Mg_5(CO_3)_4$] and hydromagnesite [$Mg_5(CO_3)_4(OH)_2$, $4H_2O$]. *Ex-situ* experiments realized by Larachi et al. (2010) on southern Québec chrysotile fibers explored low pressure, dry and moist conditions. The highest conversion rates of 0.5% were reached within 5 h at 375°C and 1 bar, which is too low an efficiency for a possible industrial application. Despite the low conversion rates, the carbonation potential of such tailings could offset a significant amount of GHG emissions.

Recent studies have mostly focused on the quantification of carbonation rates and the understanding of the parameters that can promote reaction occurring on the tailings under atmospheric conditions at the mining site (Assima et al., 2012, 2013; Assima et al., 2011; Harrison et al., 2012; Pronost et al., 2011). Nevertheless, an industrial application using mining residues could still be of value. First, there is a lack of research in direct flue gas treatment carbonation. In addition, carbonation under low temperature and pressure conditions has not yet been tested for an industrial process application. Finally, the use of south Quebec mining tailings offers the advantage of being situated close to industrial GHG emitters.

This work was conducted as part of a global research project focusing on the use of serpentinite mining residues issued from chromite exploitation to reduce post combustion industrial CO_2 emissions by mineral carbonation. As a major constraint, reaction parameters were improved with the scope to achieve the development of a process economically viable for an industrial application. Experiments were conducted in order to optimise reaction parameters such as the total pulp density the gas / liquid volumetric ratio, reaction time and particle size, to treat a cement plant like flue gas at low temperature and low pressure. In addition,`the focus is on obtaining a pure magnesium carbonate in order to obtain potential sale revenue for the reaction by-product to reduce process costs.

2. Material and methods

2.1 Sample preparation and analytical methods

Residues were collected from southern Québec in the Appalachian region, near Thetford Mines, at the old American Chrome, chromite mining site in Coleraine. Residues were sampled from surrounding rocks and thus presented heterogeneity in size. Prior to reaction, the samples were crushed using a jaw crusher and ground by an impact disc mill (*Bleuler-Mill*, NAEF) to obtain a median particle size under 75 µm. A ball mill (*Fritsch Pulverisette 6,* Oberstein, Germany) was also used for some experiments to generate smaller particle sizes. Granulometry was measured with a laser scattering Particle Size Distribution Analyzer (*Horiba LA-950V2*). Samples were heat activated in a muffle furnace (*Furnatrol 133*, Thermolyne Sybron Corporation). Solid samples were fused with lithium metaborate (*Corporation Scientifique Claisse*, Québec Canada) prior to ICP analysis.

The chemical content of solid and liquid samples was determined using ICP-AES analysis (*Vista AX CCO Simultaneous ICP-AES*, Palo Alto, CA, USA). Inorganic Carbon analyses were done with a Carbon Hydrogen Nitrogen Sulfur (CHNS) analyzer (*Leco TruSpec Micro*, St Joseph, MI, USA) on solid samples and with an Inorganic Carbon analyzer, model TOC-V CPH (*Shimadzu*, Tokyo, Japan) for liquid samples. Crystalline phases were identified by X-Ray diffraction (X-RD) analysis performed at Laval University (*Siemens D5000* diffractometer). Scans were taken for 2θ ranging from 5 to 65° with steps of 0.02°/s, with a Cu anode. Thermogravimetric analysis (TGA) was determined on a TGA 7 (*Perkin Elmer*, Waltham, MI, USA) also at Laval University.

2.2 Heat treatment

TGA analysis of the raw material indicated a major weight loss between 550 and 650°C for a total mass loss of 11.6 wt% over a period of 20 minutes. All subsequent samples were thus heat treated for 30 min at 650°C, consistent with the optimum conditions determined by Li et al. (2009).

2.3 Reaction apparatus

The experimental set up is presented in Fig.1. All the reactions were conducted in a stirred bench reactor *Model 4561* from *Parr Instrument Company* (Moline, IL, USA) of capacity 300 mL. In order to reproduce a cement plant like flue gas, a certified gas mixture composed of 4 vol% O_2, 18.2 vol% CO_2 balanced with N_2 (*Linde,* Canada) was used. The amount of solid required was weighed and added to the reactor. The desired volume of distilled water was then added and the pH measured. The vessel was closed, agitation initiated and the gas quickly injected in the reactor. When the desired pressure was reached, all valves were closed. The global pressure was not maintained during experiments, and thus decreased due to CO_2 absorption. However, pressure variation never exceeded 2.5 bar.

All experiments were conducted at 22 ± 3°C temperature with a total pressure of 10.5 bar gauge. This pressure was selected in order to maintain a sufficient quantity of gas in the reactor at the end of the experiment to enable accurate measurement of the CO_2 content. The temperature was chosen in order to maximise the CO_2 solubility in the aqueous phase (Eq. 6), which can be approximated by Henry's Law (Edwards et al., 1978). During experiments, temperature, pressure and agitation speed were controlled and recorded using a 4848 modular Controller (*Parr Instrument Company*).

After the reaction time, the gas pressure was quickly released. The exiting gas stream passed through a cold trap to condense water and then filled a sampling bag. The agitation was maintained during the gas sampling. The CO_2 concentration in the exit gas was measured with an infra-red CO_2 analyzer (*Model 906, Quantek Instrument,* MA, USA) to determine the CO_2 uptake from the gas phase. Batch wise reaction used here forced to operate at a decent pressure in order to have a sufficient amount of gas sampled. In fact no pump was used on the outline and the gas was exhausted using the vessel pressure. Below 10.5 bar, the amount of gas present after 15 minutes reaction was too low to have an accurate measurement of the CO_2 content. A mass balance on both carbon and magnesium was used to validate the results.

3. Results and discussion

3.1 Residue characterization

Chemical analysis of the residue confirmed high concentrations of magnesium, silica and iron, with a significant amount of chromium and aluminum (Table 1). The X-RD pattern identified lizardite and a crystal structure that could be either chromite or magnetite (Fig. 2). The high ratio of iron to chromium indicated in Table 1 suggests that both are present. Other crystalline phases generally encountered in ultramafic samples such as brucite, forsterite, talc or chlorite were not found. These results are consistent with the geology of the region from which the samples were taken, which is known to present ophiolitic complexes, where chromite is hosted in serpentinite (Fisher, 1929; Laurent, 1975).

The heat activation of serpentinite is known to have a very important impact on reaction efficiency (Gerdemann et al., 2003; Maroto-Valer et al., 2005; O'Connor et al., 2000). Hydroxyl groups can occupy active sites on the crystal surface inhibiting the carbonation reaction (McKelvy et al., 2004). Heat treatment removes these hydroxyl groups, allowing magnesium to be leached from the material more readily (Li et al., 2009; Nagamori et al., 1980). Serpentinite dehydroxilation is known to occur above 500°C (Béarat et al., 2006; McKelvy et al., 2004; Nagamori et al., 1980) with the simplified reaction given by Alizadehhesari et al. (2011):

$$2Mg_3Si_2O_5(OH)_4 \rightarrow 3Mg_2SiO_4 + SiO_2 + 4H_2O \tag{10}$$

XR-D observations by McKelvy et al. (2001), showed that between 600 and 800°C only an amorphous pattern was reported. That is, when the hydroxide groups are removed, the crystal structure is also destroyed. The resulting product can be considered as an amorphous magnesium silicate of approximate composition $Mg_3Si_2O_7$(Ball and Taylor, 1963). The temperature needs to be increased above 810°C, to observe recrystallization into forsterite (Mg_2SiO_4). Such recrystallization of the sample is not desired as the structural re-organization induces a decrease in the material reactivity.

3.2 Parameter optimization

3.2.1 Pulp density and Gas/liquid volume ratio (GLVR)

The effect of pulp density (the amount of solid in the liquid phase) and the ratio between the volume of gas and liquid (GLVR) were tested simultaneously. Both parameters greatly influence reaction efficiency as they determine the amount of each phase in the reactor. These parameters were optimized as function of the CO_2 uptake and the amount of magnesium leached for one 30 minute batch.

The amount of CO_2 removed from the gas phase depends upon the CO_2 solubility in the aqueous phase (Eqs. 6-7). As a base case, the mass of CO_2 in solution after contacting the gas and water was calculated in respect to Henry's law (Fig. 3). The expected CO_2 concentration in the liquid phase should be around 2.7 g CO_2/l at these temperature and pressure conditions. This value was validated through an experiment with water only at a GLVR of 3.0. As expected, the total CO_2 absorbed increases in the presence of residue. Regarding to the results with the solid, the difference between uptakes with a pulp of 5 wt% and 15 wt% is enhanced by increasing the GLVR (Fig. 3a). CO_2 uptake was similar with a 1:1 gas:liquid ratio, with 4.3 g CO_2 and 4.1 g CO_2 for 5 and 15 wt%, respectively. However, while the uptake for the 15 wt% pulp linearly increases, the uptake for 5 wt% pulp reaches a plateau at higher GLVR ratios. This indicates that in the case of a smaller quantity of solid, the CO_2 solubility can only be maintained by keeping the relative volume of liquid high. That is, having more solid helps to increase the amount of gas removed. The best uptake obtained was 0.68 g CO_2 removed representing 85% of the initial mass of CO_2, with a 15 wt% pulp density and GLVR=3.0.

The amount of magnesium measured in the liquid phase after reaction increased as the GVLR was increased for both pulp densities (Fig. 3b). This shows that acidification of the solution by CO_2 absorption is strongly linked with solid dissolution (Eqs. 7-8). The reaction mechanism would appear similar to that reported for higher pressures and temperatures (Gerdemann et al., 2007; Park and Fan, 2004) and for direct tailings carbonation (Assima et al., 2012; Harrison et al., 2012). The pulp density had little impact on the percentage of magnesium leached (Fig. 3b), but this means that a greater total mass of magnesium was extracted at the higher pulp density, with 1.07g extracted from the 15 wt% pulp at GLVR=3; relative to 0.38 g at 5 wt% pulp.

3.2.2 Sequential batch experiments

In order to increase the amount of CO_2 introduced into the reactor without increasing the global pressure, repeated experiments with four successive batches of gas were treated, each with a residence time of 30 minutes, giving a total exposure time of 120 min in the reactor (Fig. 4). From a general point of view, the increasing uptake of CO_2 with each experiment indicates that the carbonation was not limited by the solid or liquid phase, but rather by the reducing partial pressure of carbon dioxide in the gas phase as time progressed within each batch. Replenishing the gas phase allowed for more CO_2 to be absorbed and more magnesium to be leached.

These experiments highlighted the effect of the pulp density. Experiments with a 15 wt% pulp density showed a better cumulative CO_2 uptake and this uptake was reasonably linear indicating that further capacity remained even after four batches. Conversely, the CO_2 uptake with 5 wt% pulp tended to plateau suggesting that the solid phase was reaching saturation. In addition, as for assays with one batch of gas, increasing the GLVR seemed to promote reaction, as higher uptakes were observed with a ratio of 2 and 3. The best result measured was 2.15 g CO_2 removed with GLVR=2 and 15 wt% pulp density.

Fig. 5 shows the repartition of the magnesium in the liquid phase and of the inorganic carbon in the solid phase issued from the mass balance for magnesium and carbon respectively after four batches. Both data were calculated using mass balances. The percentages of Mg and C_{inorg} represent the proportion of the element in the liquid or the solid phase compared to the total mass measured in all three of the different phases. The percentage of magnesium leached into the liquid phase was higher for tests with a pulp of 5 wt%, reflecting the lower solids density; and increased with the GLVR. However, this was combined with a lower percentage of carbon in the solid after reaction. These observations were not consistent with those for one batch, as in this earlier case, the pulp density had no effect on the amount of magnesium in the liquid phase. Nevertheless, for GLVR =1 and 2, the amount of inorganic carbon measured in the solid phase was significant, respectively 68 wt% and 37 wt%. In addition, the mass of solid obtained after reaction was higher than the mass originally added for these tests. These results suggest that Eqs 7-8 continue until the solution is saturated with HCO_3^- and Mg^{2+} and this leads to precipitation of solid magnesium carbonate ($MgCO_3$). Magnesium silicate dissolution (Eq. 8) is known to be rapid due to proton transfer on the mineral surface (Luce et al., 1972; Nagy, 1995;

White and Brantley, 1995). The larger total amount of solid introduced for the GLVR=1 and 2 tests induced greater quantities of these silicates in the liquid phase, which facilitated carbonate precipitation despite the slow kinetics at these temperature conditions (Hänchen et al., 2008; Wells, 1915). This carbonate precipitation allowed more CO_2 to be dissolved and could explain the lower CO_2 uptake observed at GLVR=3 compared to GLVR-2 with 15 wt% pulp (Fig. 4). However, given the importance of producing a pure carbonate having a potential sale value, carbonate precipitation in the reactor is not desired. It was thus decided to continue experiments with a GLVR of 3 and 15 wt% pulp density which appeared to be the best conditions for the reaction under the experimental temperature and pressure conditions.

3.2.3 Reduction of the reaction time

A series of tests was also conducted in order to see if the reaction time could be reduced. Each point presented in Fig. 6 corresponds to a unique run, with fresh solid residue. The CO_2 uptake significantly increased from zero to 56% after 5 minutes and to 83 % at 10 minutes but then slowed to reach 90% after 25 min. The amount of magnesium leached showed a quite similar pattern, so that after 15 min both CO_2 uptake and magnesium leaching presented acceptable values. In light of these results, reaction time was thus reduced to 15 min.

3.2.4 Particle size

The previous experiments were performed with particles having a median size around 75 µm. A series of tests were also conducted with samples prepared using a ball mill for one, two or three grinding cycles of three minutes each. Particle size analysis showed that after two cycles, the mean and the median size of the sample were reduced by more than a factor of three (Table 2), while a third grinding cycle had little effect. This could be explained by the fact that the smaller particle size material sticks to the ball and thus lowers the mill efficiency. In addition, Kim and Chung (2002) report agglomeration of fine serpentine particles after long grinding times, which may also have influenced our measurement.

Even though the specific surface area increased significantly with grinding, the CO_2 uptake and the magnesium leached were unaffected (Table 2). This is consistent with the discussion in Section 3.2.2 and Fig. 4.

That is, it is the low partial pressure of carbon dioxide that limits further reaction within any batch, rather than the availability of solid reacting surface. A smaller particle size would have more impact on the efficiency of successive batches where more CO_2 is introduced and surface limitations may become rate controlling.

3.3 Successive batches and recirculation scenario

The parameter optimization confirmed that one of the limiting factors was the amount of CO_2 introduced in the reactor. This could be increased by increasing the global pressure in order to increase the partial pressure of CO_2. Assays realized in high pressure conditions revealed that the amount of CO_2 treated and Mg dissociated from the solid were increased. However, operating at higher pressure is expensive to achieve in an industrial setting and has safety concerns. The other option was to treat the same solid material with successive batches of gas and to also refresh the liquid phase. Specifically, in order to reduce saturation of the liquid phase known to limit reaction in these conditions (Werner et al., 2013). In a more practical application, this can be removed from the reactor and transported to a separate unit where magnesium carbonate can be precipitated by increasing the temperature around 40°C in order to increase precipitation kinetics (Hänchen et al., 2008). At an industrial scale, the remaining liquor might then be at least partially recirculated, once the carbonates have precipitated. Such a scenario would require further development as the remaining Mg in the liquid phase will limit reaction. In the present case, we consider the use of fresh water for successive batches, rather than recirculated liquor.

The following scenario was tested. A pulp was contacted with two successive batches of gas for 15 min. each and then filtered. The resulting filter cake was mixed with fresh water and returned to the reactor to react with two more successive batches of gas. For the first series of tests, the solid was recirculated three times for a total of six batches of gas treated. A total of 12 assays were realized. CO_2 uptake was maintained at around 0.68 g CO_2 per batch for the first three batches and then decreased to reach 0.41 g CO_2 treated for the 6th batch (Fig. 7). The cumulative uptake showed a linear increase until the 5th batch and then slightly decreased for batch 6. The total CO_2 removed from the gas was 3.61 ± 0.09 g CO_2 after six batches for an average uptake efficiency of $76 \pm 2\%$. Changing the liquid phase after each two batches of gas, helped to increase the amount of CO_2 removed. In addition, the amount of carbon measured in the solid phase after reaction was not significant showing that no precipitation occurred in the reactor. On the other hand, the liquid phase was concentrated in magnesium, with respectively 14 ± 1%, 14 ± 1% and 11 ± 2% of the total magnesium leached after two, four and six batches of gas treated. The total amount of magnesium dissolved reached 34 ± 3% (0.95 g Mg measured in the liquid phase for 2.81 g Mg initially measured in the solid). Assuming that all the magnesium contained in the liquid phase will be then precipitated in the downstream vessel, the g CO_2 treated/g of residue was 0.32 (3.61 g CO_2 for 11.25 g of solid).

Further runs were performed to treat more gas. The decreasing trend in the efficiency observed after the 6th batch (Fig. 7) was confirmed by performing two more batches on the solid ("Normal" Table 3). The CO_2 uptake showed a slight increase due to the utilization of a fresh liquid fraction for batch 7 but decreased to 0.25 g CO_2 at the 8th batch. In addition only 4 wt% of magnesium was dissolved from the solid. These results suggest that inhibition of the surface occurred due to the accumulation of a non-reactive material on the grain surface (Béarat et al., 2006; McKelvy et al., 2004).

Different treatments were performed on the solid obtained after treating six batches of gas in order to reduce this surface passivation layer. Table 3 presents results obtained for Batch 6 before each treatment and for Batches 7 and 8 after material reconditioning.

The addition of sulfuric acid to the reactor should assist the magnesium leaching from the solid (Alexander et al., 2007). However, the lower pH of the solution will retard CO_2 solubility by pushing Eq 7 to the right (Chen et al., 2006; Park and Fan, 2004; Stumm and Morgan, 1996) In all earlier experiments, the pH measured directly after mixing the solid in solution was between 10 and 11, and decreased to around 7.5 after reaction, induced by CO_2 dissolution. Here only a very small amount of acid was added, in order to maintain a sufficient CO_2 solubility by keeping the pH above 7. Nevertheless, conditions were not favorable for CO_2 uptake and the amount of magnesium leached was low.

McKelvy et al. (2006) reported that the addition of 60 wt% of quartz helped the carbonation of olivine at high temperature and low pressure. In our case, the addition of SiO_2 did not create sufficient attrition, to physically reduce the passivation layer. Results obtained were in the same range as those obtained without any treatment.

On the other hand, both a second heat treatment of the material and the use of ring mill grinding showed more interesting results. Best results were obtained for a material which was ground and then heat treated. CO_2 uptake was increased compared to that observed after six batches, and magnesium leaching was around the values obtained with a fresh material. Grinding the material helped to break the passivation layer on the material surface. In addition, Kim and Chung (2002) related that long grinding sequences on serpentine disturbed the crystal structure creating an amorphous material and thus increasing the serpentine reactivity. Our grinding time was much lower, but the addition of the heat treatment allowed increased material reactivity. Around 8 wt% of the mass was lost during the second heat treatment of the material. TGA analysis showed that about 5% of the mass was lost after reaching 300°C, which was due to water removal and possible de-carbonation. A total of 3% of the mass were lost between 500°C and 750°C showing that dehydroxilation of the material was still possible. On the other hand, it showed that the efficiency of the first heat treatment was not maximized.

As grinding and further heat treatment after six batches of gas gave positive results, tests were performed to treat 12 batches of gas with reconditioning of the solid after six batches. The same scenario as described for the six first batches of gas was followed (renewing water after two successive batches of gas treated). A total of 5.86 g CO_2 was treated with the same solid reconditioned after six batches. Another scenario where the solid sample was ground and heat treated after batches 7 and 9 was also tested. It appeared that only a re-treatment after six batches was necessary as no improvement was measured in this latter case

The final overview of the efficiencies on the CO_2 uptake and the amount of magnesium leached from the solid is showed in Table 4. Triplicate assays were realized. From a general point of view, results were in accordance with those previously observed. The amount of gas treated and the magnesium leached from the solid slightly decreased among the first six batches. The reconditioning of the solid allowed the CO_2 uptake to be maintained at up to 0.4 g CO_2 until Batch 11. After twelve batches of gas treated, a total of 6.14 g CO_2 had been consumed for a cumulative CO_2 uptake efficiency of 62.5 ± 0.5%. The mean percentage of magnesium leached from the solid over the three replicate runs performed was 64 ± 7%. By assuming that all the removed CO_2 is then precipitated, the ratio of CO_2 treated is 0.55 g CO_2 per g residue. This is higher than reported maximum capacity for similar material. Such increase is here linked with the uptake generated by the water only, which was cumulated due to regular liquid changes. Compared with the capacities reported by Bobicki et al. (2012) for different types of alkaline wastes, this ratio is very interesting as the amount of solid material needed for the treatment is reduced.

4. Industrial application

The use of natural minerals such as serpentine as a media for direct flue gas CO_2 reduction is so far not well documented. Reduced CO_2 partial pressures encountered in these conditions requires to operate in modified conditions compared to those reported in the literature for the treatment of a concentrated CO_2 stream. In fact, conditions are closer from natural weathering conditions reported on mining residues. While energy requirements for the carbonation reaction are lowered compared to high temperature and pressure conditions, material preconditioning requirements still stand as major energy inputs. Considering an industrial application of the reaction described here with a treatment capacity of 200 t of rocks per hours, a total of 585.55 kWh/t of rocks is required for the two heat activation steps. Nevertheless, the first heat treatment efficiency may be increased in order to avoid one. For example, the application of N_2 gas flow in order to increase water removal from the crystal surface which limit the dehydroxilation efficiency (Candela et al., 2007). Particle size reduction is also standing as an important energy input. Both grinding step were estimated to require 28.44 kWh/t of rock. Compared with energy requirement described for magnetite ore extraction where similar granulometry are encountered (McNab et al., 2009). The application of concurrent grinding (Werner et al., 2013), or attrition (Gerdemann et al., 2007) instead of a grinding step could be considered as options for solid reconditioning to reduce surface limitations. So far, precipitation efficiencies were around 60% after 3 hours at 40°C reducing the sequestration potential to 0.33 g CO_2 sequestered per g of residue. In addition, the size of such equipment for a plant with a capacity of 200 t rocks/h is estimated at 19 x 10^3 m^3 requiring 583 kWh/t of rocks with an energetic efficiency of 80% to heat up the solution at 40°C. Energy requirements could be offset by the recovery of heat from the flue gas cooling required prior to the carbonation reaction. Nevertheless precipitation is sensitive as it drives the amount of CO_2 sequestered, and magnesium carbonates could stand as a major income for the process costs balance. With a market price ranging from 250-360 $/ton depending of the grade purity (Kramer A.D., 2001), the production of a pure carbonate represent a very important point regarding a possible industrial application. In addition, results described here were obtained with a global pressure of 10.5 bar due to experimental limitations. To be more practically feasible, the pressure operation should be decrease, which in continuous gas flow would be achievable with residence time adaptation to maintain a high CO_2 dissolution.

5. Conclusion

The optimisation of reaction parameters for the use of mineral carbonation in the aqueous phase for direct flue gas CO_2 treatment has been developed. Relative to prior work in the field, reaction temperature and pressure conditions were significantly lowered and the gas composition modified to suit the low CO_2 concentrations encountered with a flue gas. In addition, the desire to precipitate pure magnesium carbonate as a saleable by-product led to the use of refreshing of the aqueous phase as a process strategy. The amount of CO_2 introduced into the reactor drove CO_2 uptake and magnesium leaching efficiencies. Nevertheless, increasing global pressure was avoided by contacting the same pulp with two successive batches of gas for 15 minutes each. The slurry was then filtered in order to obtain a saturated solution of magnesium carbonate. The solid was mixed with fresh water, and again contacted with more gas, while magnesium carbonates where precipitated from the solution in a separate reactor. In addition, passivation layer inhibition was reduced by performing a second grinding and a second heat treatment on the residues. In the end, renewal of the liquid phase to limit saturation, and a single regeneration of the residue in the middle of the process facilitated a significant carbon dioxide uptake. In this manner, carbonation efficiencies equivalent to those reported with high temperature and pressure conditions were achieved. With extended work on energy efficiency and magnesium carbonate precipitation, the application of a process using serpentinite based minerals residues could stand as a promising industrial CO_2 reduction technology.

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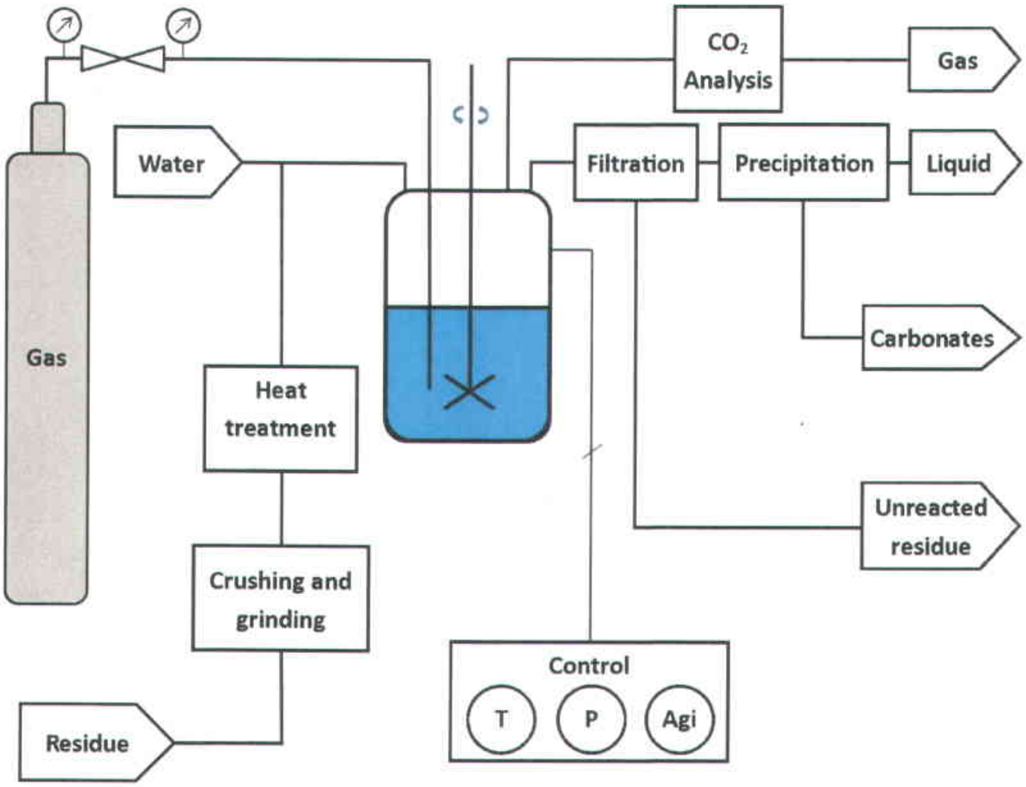


Fig. 1. **Schematic presentation of the experimental set-up**

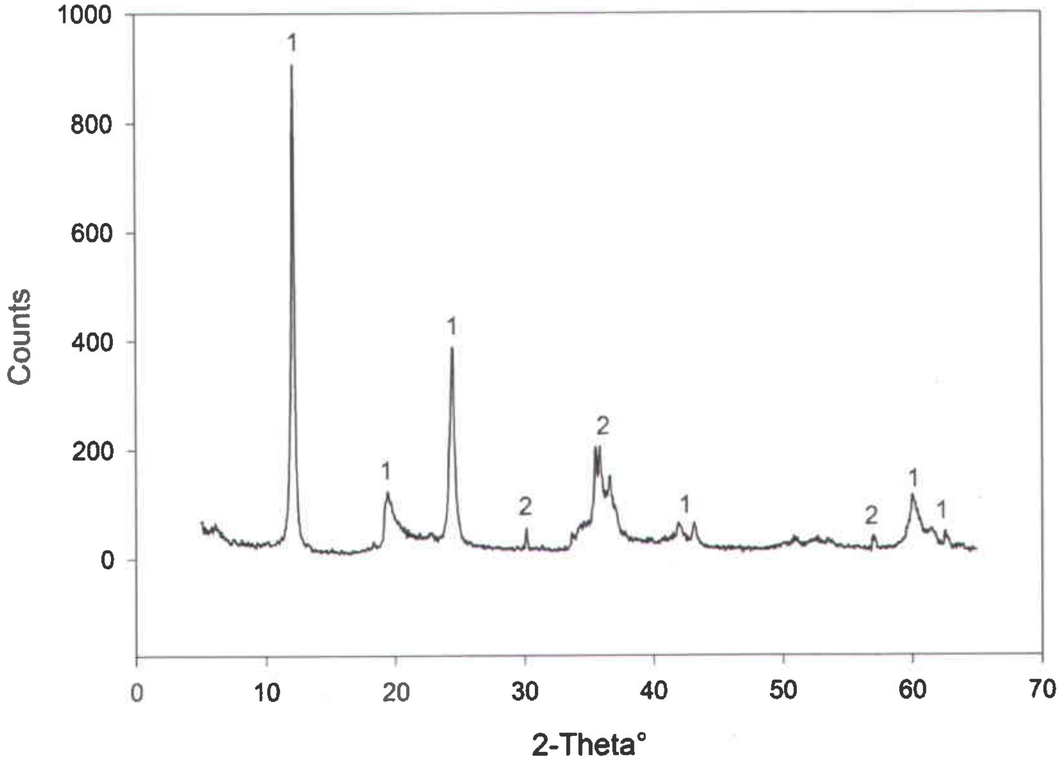
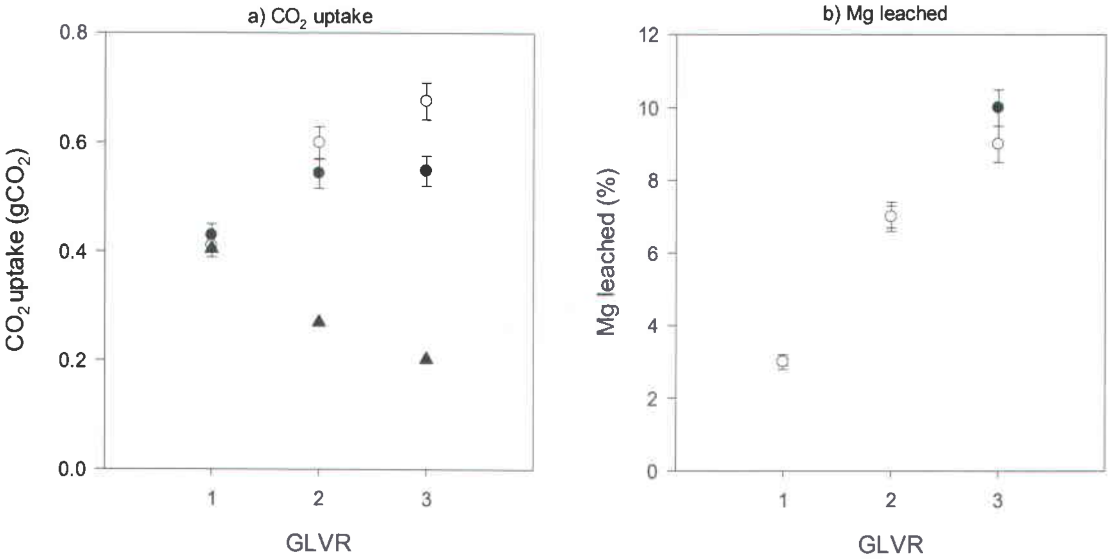


Fig. 2. X-RD pattern of the raw residue in the 5-65° region. (1) Lizardite, (2) Chromite and/or Magnetite



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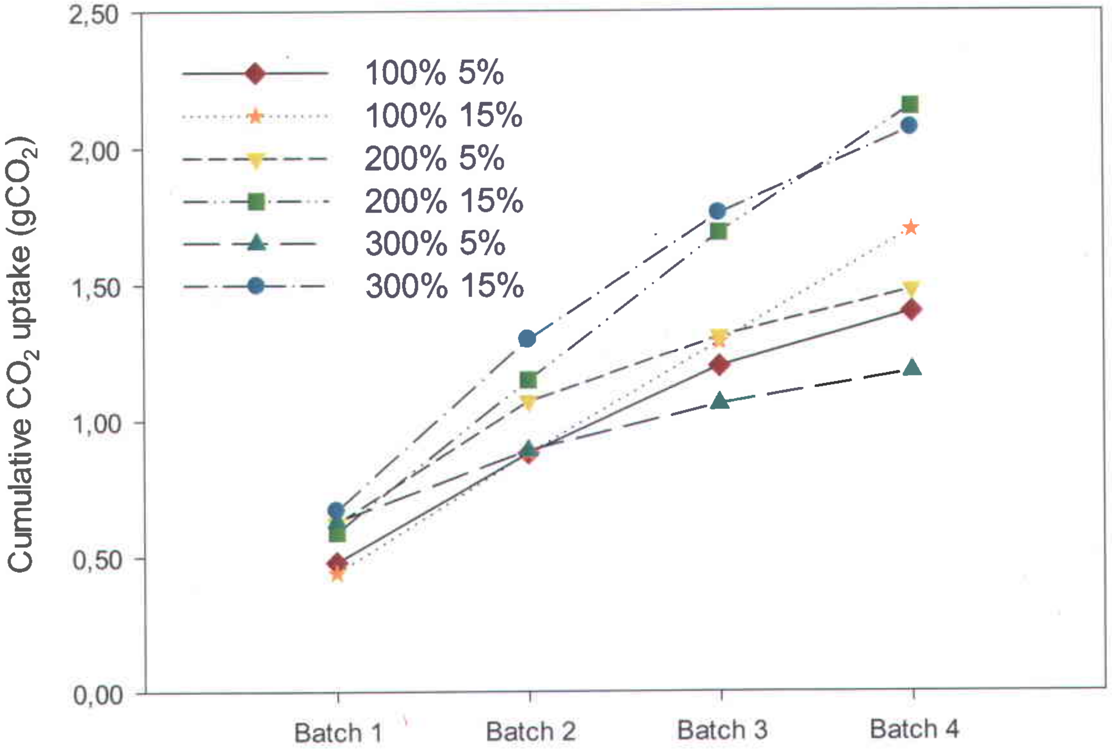
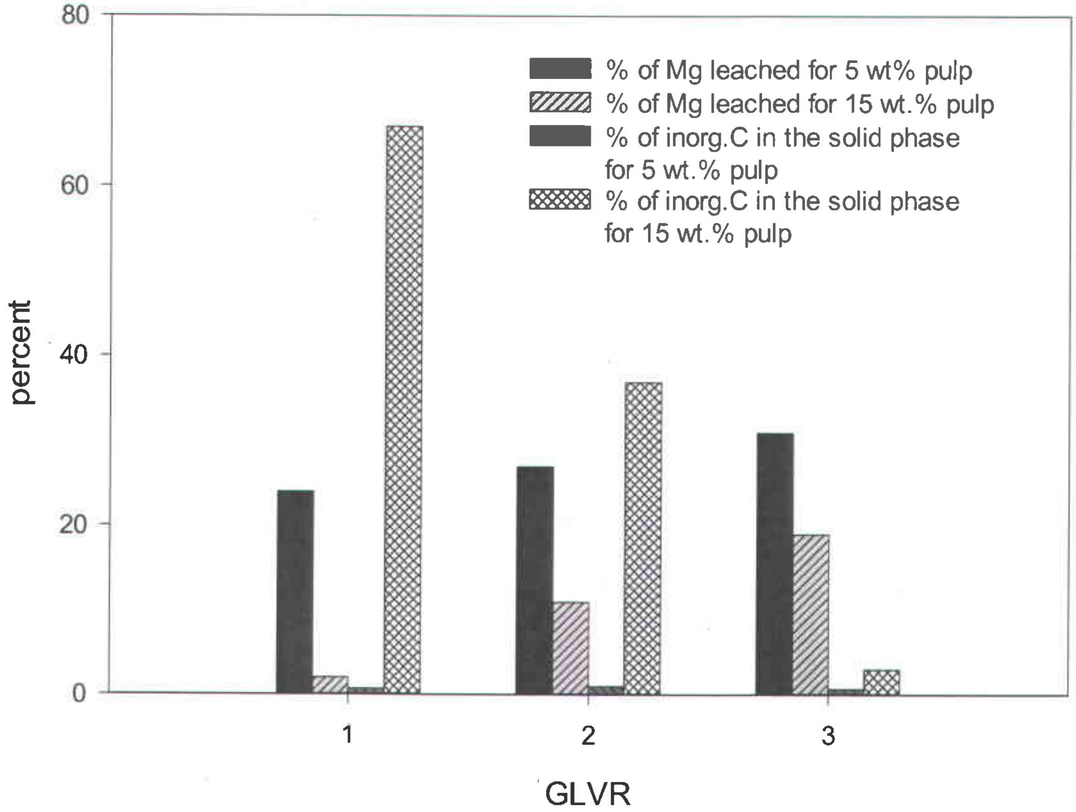


Fig. 4. Cumulative CO$_2$ uptake in g of CO$_2$ treated for four successive batches. Effect of the GLVR (1.0, 2.0 and 3.0) and the pulp density (5 and 15wt.%)



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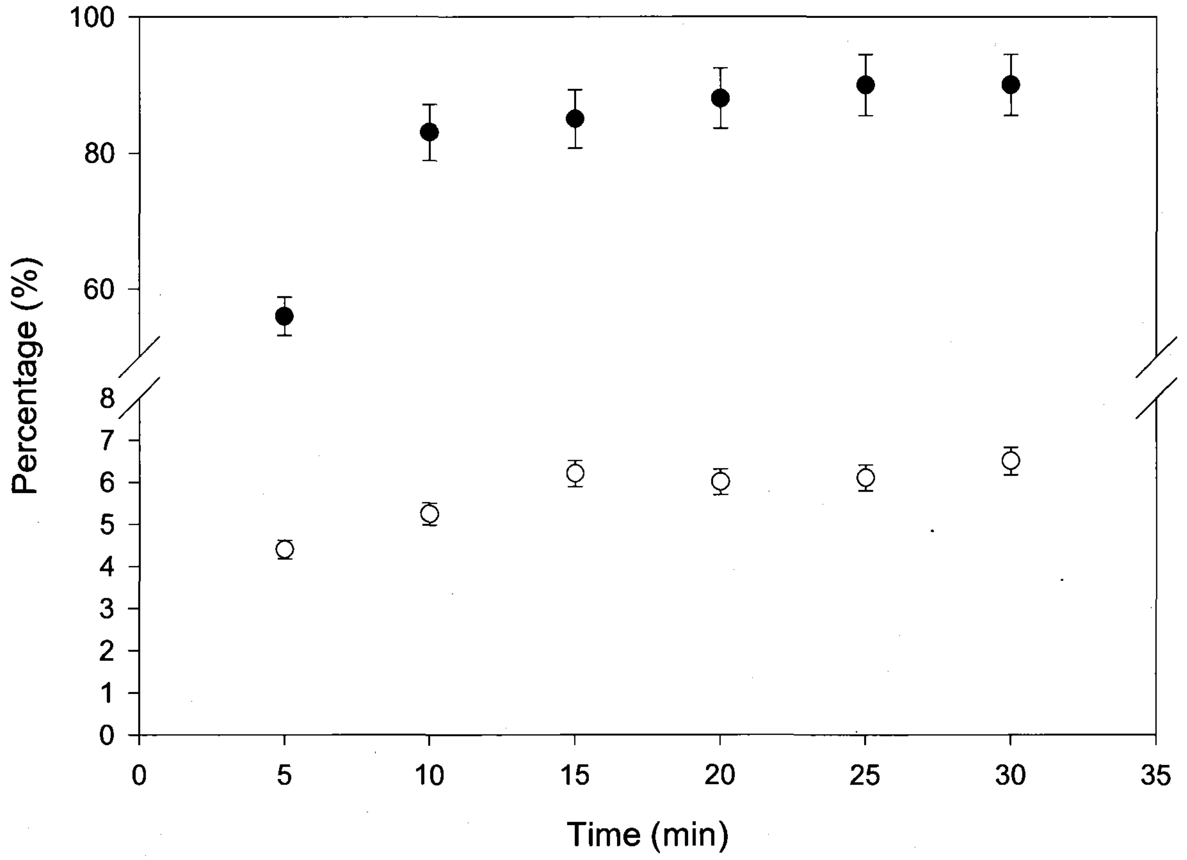

Fig. 6. CO$_2$ uptake (●) and amount of Mg leached from the solid (○) as function of time. Errors bars stands for 5% error.

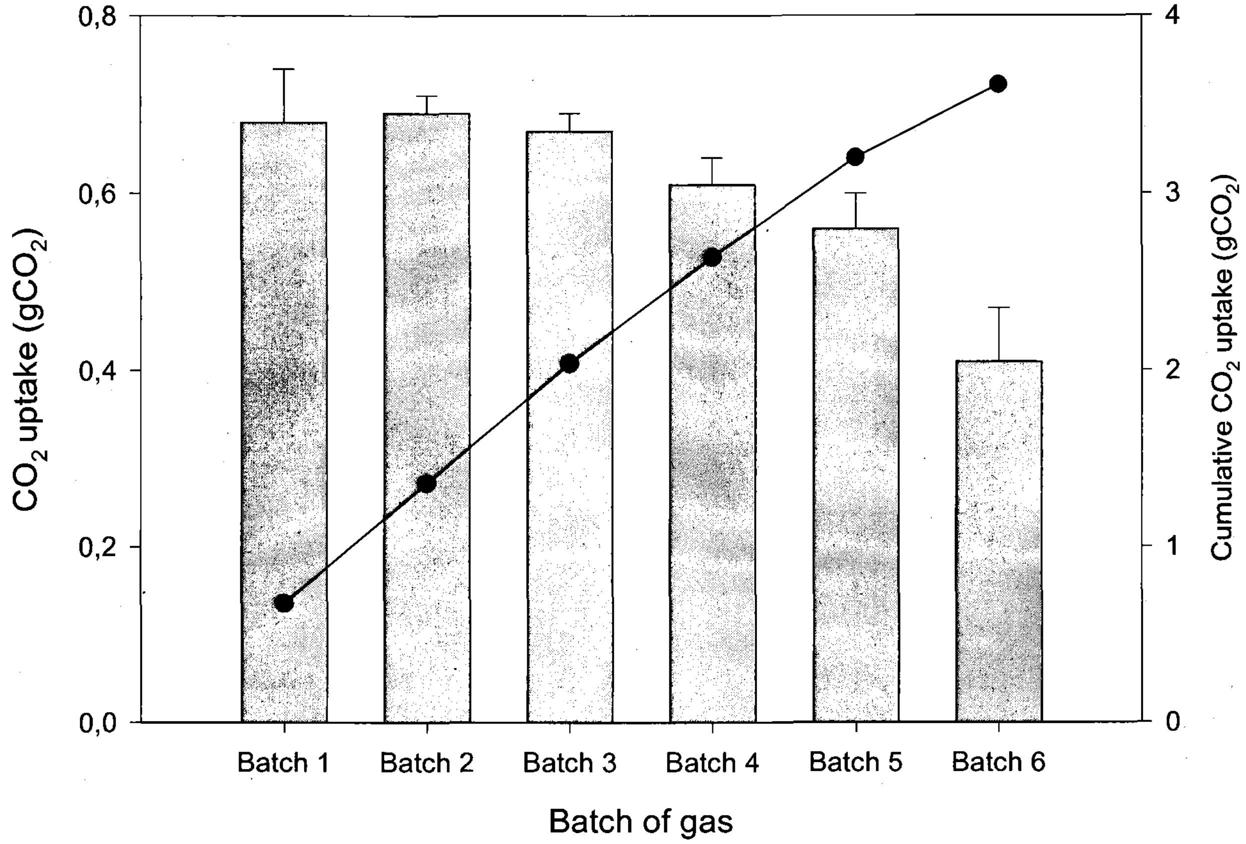

Fig. 7. **Average (bars) and cumulative (●) CO_2 uptake measured after each batch of gas for six successive batch treatment at 10.5 bars, ambient temperature and 15 wt% pulp density. Error bars stands for standard deviation (*n* = 11).**

Table 1

Chemical composition of the raw residue.

Elements	Units	Values
Al_2O_3	wt%	1.6
CaO	wt%	0.04
Cr_2O_3	wt%	0.9
Fe_2O_3	wt%	19
MgO	wt%	47
MnO	wt%	0.05
SiO_2	wt%	42
C_{inorg}	wt%	0.24
LOI [a]	wt%	11.6

[a] Lost on ignition.

Table 2

Effect of the number of grinding cycles on particle size, specific surface area, CO_2 uptake and Mg leached after 15 min of reaction (*n* = 3)

Grinding cycle	Mean size (μm)	Median size (μm)	Estimated specific surface area (m^2/kg)	CO_2 uptake (g CO_2)	Mg leached (%)
1	137 ± 27	55 ± 22	2341 ± 176	0.73 ± 0.05	7.0 ± 0.2%
2	45 ± 9	16 ± 5	4874 ± 997	0.75 ± 0.07	6.9 ± 0.6%
3	43 ± 10	12 ± 1	6352 ± 389	0.74 ± 0.03	6.9 ± 0.1%

Table 3

Effect of different treatments on the solid after the treatment of six batches of gas on CO_2 uptake and Mg leaching for 7 and 8 batches of gas treated.

Treatments	Batch 6		Batch 7		Batch 8	
	CO_2 (g)	Mg (% sol.)	CO_2 (g)	Mg (% sol.)	CO_2 (g)	Mg (% sol.)
Normal	0.335	10%	0.403	-	0.249	4%
H_2SO_4	0.314	7%	0.272	-	0.163	3%
Quartz	0.314	9%	0.389	-	0.252	3%
Heat treatment	0.375	9%	0.423	-	0.300	7%
Grinding	0.443	13%	0.540	-	0.368	11%
Grinding + Heat treatment	0.443	13%	0.549	-	0.541	16%

Table 4

Efficiencies for CO_2 treated and Mg leached for 12 batches of gas treated by one solid (*n* = 3)

Batch	Gas treated (g CO_2)	Mg leached (%)
1	0.68 ± 0.06	
2	0.69 ± 0.02	14 ± 1
3	0.67 ± 0.02	
4	0.61 ± 0.03	14 ± 1
5	0.56 ± 0.04	
6	0.41 ± 0.06	11 ± 2
7	0.44 ± 0.05	
8	0.59 ± 0.05	15 ± 1
9	0.53 ± 0.02	
10	0.42 ± 0.01	7 ± 1
11	0.27 ± 0.01	
12	0.29 ± 0.01	4 ± 1
Total	6.14 ± 0.36	64 ± 7

CHAPITRE 4 : ARTICLE 3

Economic evaluation and feasibility of a mineral carbonation process using southern Québec mining waste for direct flue gas CO_2 sequestration with by product recovery.

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RÉSUMÉ

La carbonatation minérale est une des méthodes de séquestration du CO_2 les plus sûres. Cependant, la plupart des technologies proposées ne sont pas viables économiquement. Plusieurs approches ont été testés afin de réduire les coûts de procédés, mais peut ont étudiée la faisabilité d'un traitement direct à la cheminée d'un gaz de combustion, privilégiant le traitement d'un gaz concentré en CO_2. Cette étude s'intéresse à l'utilisation de résidus miniers composés de serpentinite activés thermiquement comme matériel de séquestration. La réaction est réalisée dans un réacteur agité à basse température et basse pression afin de traiter un gaz contenant 18.2 vol.%. L'optimisation des paramètres a conduit à l'élaboration d'un scenario de recirculation où 64% du Mg initialement contenu dans les résidus est dissout après 3h. Le temps de rétention du gaz est quand-a lui de 15 minutes, et un enlèvement cumulé de 65% est obtenu lors du traitement de batch successives. De plus, afin de réduire la saturation de la solution, celle-ci est remplacée périodiquement. Une fois filtrée, des carbonates de magnésium sont précipités à partir de celle-ci, sous forme de nesquehonite ($MgCO_3.3H_2O$) quasi pure. Les conditions douces de réaction offre ainsi une nouvelle perspective pour l'application d'un tel procédé pour la réduction d'émissions de CO_2 issues de l'industrie. Cette étude s'intéresse au bilan économique du procédé décrit en comparant différents scénarios impliquant différents modes de transport et différentes sources d'énergie pour l'activation thermique des résidus. Les coûts généraux du procédé varient de 129 à 97US$/t$CO_2$ traité en fonction du scénario considéré. L'étude de profitabilité démontre qu'une telle approche est rentable, grâce aux revenus générés par la vente de carbonates de magnésium et par le crédit carbone. Sur une période de 10 ans, le profit net actualisé varie de 124 à 236 M US$ avec une période de retour sur investissement inférieure à 5ans. Le bilan des émissions de GES est également présenté.

Mots Clefs: Carbonatation minérale, Résidus miniers, Traitement d'un gaz de combustion, Évaluation économique.

ABSTRACT

Mineral carbonation is one of the safest ways to sequester CO_2. However, most of the proposed technologies to date have had difficulty in achieving an economic return. Different approaches have been tested in order to reduce processing costs. Nevertheless, few studies have considered the possibility of a direct flue gas treatment, preferring to focus on reaction with a concentrated CO_2 gaseous stream. In this work, a process using heat treated serpentinite extracted from mining residues was developed. Reaction takes place in an aqueous phase stirred reactor, at low temperature and relatively low pressure, in order to treat a gas containing 18% CO_2. Optimization has resulted in the selection of a recirculation scenario, where 64% of the Mg originally introduced is dissolved and reacted in 3 h. On the other hand, the residence time of the gas is reduced to 15 min, and a cumulative CO_2 uptake of 65% can be achieved within a 3 h reaction period. In addition, in order to reduce solution saturation, the aqueous phase is periodically replaced. Magnesium carbonates are then precipitated from this aqueous phase as pure nesquehonite ($MgCO_3.3H_2O$). The mild operating conditions and by-product recovery offer a new perspective for the application of mineral carbonation to reduce industrial CO_2 emissions. Depending upon the transportation mode and the source of energy for the heat activation, the process costs vary from 129 to 97 US$/t CO_2. A profitability analysis shows that the overall approach is profitable due to income generated by the sale of reaction by-product and carbon tax benefits balancing these process costs. Over a 10-year period, the NPV value ranged from 124 to 236 M US$ depending upon the scenario, with a payback period less than five years. The greenhouse balance is also described in order to have a global discussion of the feasibility of such a CO_2 sequestration technique.

Keywords: Mineral carbonation, Mine waste, Flue gas treatment, Economic evaluation

1. Introduction

In his last report for policymakers, the Intergovernmental Panel for Climate Change (IPCC) confirmed that the increase of greenhouse gases (GHG) emissions was linked with observed changes in climate (IPCC, 2013). Worldwide efforts to reduce emissions should undeniably lead to restrictive legislation in order to achieve emissions targets. The province of Québec joined in 2008 the Western Climate Imitative (WCI), which also includes the provinces of Ontario, Manitoba, British Columbia (Canada) and the state of California (USA) in implementing a cape and trade system in order to reduce GHG emissions (Gouvernement du Québec, 2013b). Since the beginning of 2013, over 80 facilities from the industrial and the power generation sector are required to comply with GHG emissions regulations. Significant emitters must find solutions to reduce their emissions to avoid binding carbon taxes.

The integration of a CO_2 sequestration process in order to treat post combustion gaseous emissions represents a major challenge in terms of GHG reduction. Two types of sequestration could be applied. Capture processes will remove and concentrate CO_2 to provide a "pure" stream for long term storage within a geological formation. On the other hand, a process involving mineral carbonation can provide both capture and sequestration at the plant. The gaseous stream is reacted with solid material containing divalent cations such as calcium and magnesium, in order to bind CO_2 to form carbonates. Such reactions can be realized in both aqueous and dry conditions. Nevertheless, while mineral carbonation offers a safe sequestration solution, the reaction kinetics can be unreasonably slow (IPCC, 2005). The resulting increased operating costs stand as a major disadvantage for an industrial application.

One of the first works published on aqueous mineral carbonation was conducted by Lackner et al. (1995) who suggested the approach as an alternative to geological sequestration. Later work by (Huijgen, 2003) focused on reacting a supercritical pure CO_2 stream under aqueous conditions in order to produce stable carbonates. Reactions were conducted with pure minerals such as olivine serpentine and wollastonite at high pressure and temperature. The costs associated with feedstock mining and extraction, preconditioning (grinding and milling), thermal activation in the case of serpentine and the extreme operating conditions resulted in uncompetitive economics (O'Connor et al., 2005; Sipilä et al., 2008). Nevertheless, research continued and looked for alternatives in order to increase efficiencies and to reduce operating costs. Among these options, the use of alkaline industrial wastes such as cement kiln dust, steel slag or mining tailings was shown to offer opportunities as a more readily reactive feedstock, which in some cases, was already finely ground (Bobicki et al., 2012). With such an approach, the impact of solid material preconditioning could be avoided or reduced. To date, direct flue gas mineral carbonation has been the major focus, with calcium containing feedstocks (Gupta and Fan, 2002; Uibu et al., 2011) and under dry conditions (Zevenhoven et al., 2002). Nevertheless, heat treated serpentinite has also proved to be an interesting media for aqueous mineral carbonation at low CO_2 partial pressures (Werner et al., 2013).

Mineral carbonation costs, based on treatment with a pure CO_2 stream, have been estimated to be between 50 and 100 US$/t CO_2 (IPCC, 2005; Lackner, 2002; O'Connor et al., 2005; Penner et al., 2004). However, such cost evaluations generally do not take into account the price of a capture step (Herzog, 2002). However, post combustion industrial gases contain low concentrations of CO_2. The costs associated with concentration of this carbon dioxide prior to the carbonation step have an important impact on the global processing economics. Despite technology improvements, amine capture process costs can range from $US 52 to 61 per tonne of CO_2 avoided (NETL, 2012). This cost needs to be added to the overall cost of sequestration.

The Québec province is unique due to the large quantities of mining tailings generated by chrysotile asbestos exploitation in the southern region (Fig. 1). Estimates have shown that the 2 Gt of Mg silicates residues available in this province could sequester 625 Mt of CO_2 (Huot et al., 2003). Natural carbonation of such tailings is known and a number of studies have been conducted in order to measure and increase the direct carbonation of the tailings (Assima et al., 2012, 2013; Beaudoin et al., 2008; Power et al., 2010; Pronost et al., 2011; Wilson et al., 2009; Wilson et al., 2006). Recent studies have shown that such natural carbonation rates may have been underestimated and that this process could offset the GHG generated by the mining operations (Harrison et al., 2012). In addition, the economic study presented by Hitch and Dipple (2012) showed that the implementation of a sequestration process using the carbonation of such residues to offset emissions was financially feasible with the establishment of a cap and trade system. While exploitation of chrysotile fibers in the Quebec province is slowly coming into an end, the residues still stand as a potential sequestration media due to the advantageous geographic situation of the tailings compared to large emission sources (Fig. 1).

This article focuses on the economic evaluation of the process developed by Pasquier et al. (2013) where heat treated mining residues are used for reducing CO_2 emissions from industrial flue gases. The GHG balance for the overall process is also determined. This paper does not pretend to present an exhaustive analysis. Nevertheless, it identifies potential economical weak points regarding the implementation of such a process at an industrial site within Quebec, and provides guidance for the development of mineral carbonation as a viable sequestration technique elsewhere in the world.

2. Methodology

2.1 Process diagram

This study focused on the use of mining residues from the Thetdford-Mines and Asbestos area (point A and B, Fig. 1). As previously described, the history of the region was mainly focused on the exploitation of chrysotile asbestos. On a smaller scale, chromite was also extracted in the area. Thus the composition of the residues varies depending on the location. The parameters used for the simulations were taken from experiments conducted with residues extracted from the old chromite exploitation American Chrome (Pasquier et al., 2013). Most of the residues from this area contain magnetite and other magnetic minerals (Laurent, 1975). Such material is not necessary for the mineral carbonation and can be an inhibitor for material dissolution (Assima et al., 2012). In addition, such material can present a potential sale value giving additional financial income to the project. Thus, after crushing and grinding, the magnetic fraction of the solid feedstock is removed prior to the mineral carbonation step (see Fig. 2).

In the model, this step was performed using electromagnetic separators, although a gravimetric/particle size separator such as spiral or hydro-cyclones could be used. It is also plausible to have separate milling steps before and after the magnetic separation, depending upon the final particle size requirements. It is possible that the crushers and the mills are still operational at the old mining site. Nevertheless, the base case scenario takes into account the purchase of this equipment.

Transportation of the residual rock (principally serpentinite) from the mining site to the emission source occurs after milling and magnetic separation. Train routes exist in the southern Quebec region near the tailings, and often the industrial emission sources presented in Fig 1 also have train facilities. The use of serpentinite as the sequestration media requires thermal activation, in order to obtain sufficient carbonation efficiency (O'Connor et al., 2005). While this step is known to be costly in terms of energy, the use of waste heat from the industrial emission source may be possible. Again, to be more conservative, this study did not consider any heat integration with the emission source. Rather the use of either natural gas, or a local supply of residual biomass is considered.

The study focuses on the use of an 18 vol.% CO_2 flue gas, which is close to that from a typical cement plant. The gas prior to reaction with the solid is cooled by heat exchanger and compressed. The mineral carbonation process is the same has described by Pasquier et al. (2013). Two gas treatment steps (GT1 and GT2) are used. Each step includes three successive stirred continuous flow reactors, with the gas and the solids flowing through each reactor in turn. Compared with laboratory assays, the reactors are operated in co-current flow. Nevertheless, a counter-current operation could also be considered as it may enhance reaction rates. The retention time (RT) of the gas within each reactor was fixed at 15 min. The concentration of solid in the pulp is 150 g/l with a gas/liquid ratio of 300%. The global pressure is fixed at 10.2 bar and the temperature set at 25°C. As the process requires re-activation of the material to reduce limiting surface passivation, the solids content is then separated by centrifugation. The resulting concentrated liquor, containing dissolved magnesium carbonates (CCE) is send to the precipitation unit, while the solid is milled, and heat treated prior to the second carbonation unit (GT2) where the same operating parameters as described for the GT1 are applied. The pulp is again separated by centrifugation. The resulting solid is considered as non-reactive and discarded for example into the open pit created by the calcite exploitation in the case of a cement plant or a limestone plant. The resulting liquid phase is placed in the precipitation unit.

Precipitation of Mg carbonates is known to be controlled by kinetics and is thus favored at elevated temperatures (Hänchen et al., 2008). On the other hand, increasing temperature would also lead into a major CO_2 depletion from the solution, due to a reversal of the carbonation equilibra. Based on equilibrium calculations, the temperature of precipitation was set at 40°C, were CO_2 losses were limited. Lab experiments showed that 90% of the Mg in solution could be precipitated within 18 h. However, in a continuous crystallisation process, where fresh concentrated solution is continuously added to maintain the total concentration above the saturation point and considering the seeding effect created by the carbonates already precipitated (Benefield and Morgan, 1990), the residence time is more likely to be of the order of 120 minutes. Once precipitated, the carbonates are dried and sold. This last point is possible as the precipitation takes after separation from the solid feedstock, giving an almost pure nesquehonite. This point will be discussed later, but the potential sale value of the carbonate represents a major financial income.

2.2 Cost modeling

The financial analysis was based on a mass balance calculated from the global reaction of serpentinite carbonation (Eq. 1).

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \rightarrow 3MgCO_3 + 2SiO_2 + 4H_2O \qquad (1)$$

The base case cost was determined using parameters and efficiencies for the mineral carbonation reactions (GT1 and GT2) observed during lab scale experiments. All mass balance calculations were based on the treatment of 200 tonnes of rock per hour. The cost calculation considered major operating costs such as labor, utilities, which includes electricity, process water, energy (here natural gas or biomass), rock transportation and loading. Equipment included, screw conveyors for moving solids, diaphragm pumps for moving liquids, centrifuges for separating liquid and solids. Compressors situated before both series of three successive stirred reactors move the gas. Rocks heat treatment is realized using two successive rotary kilns with a maximum capacity of 63t/h each, milling is performed by mills with a maximum capacity of 625 t/h and magnetic separation with wet high intensity magnetic separators. Liquids and solids are stored in carbon steel tanks. Reaction between the gas and the pulp take place in stirred carbon steel reactors having a capacity of 2274 and 1415 $m^3$for GT1 and GT2 reactions steps respectively. Magnesium carbonates precipitation is realized in two 6268 m^3 carbon steel tanks. The flue gas cooling is realized by a shell tube (floating head) heat exchanger with a exchange surface of 606 m^2. The gas is then compressed in six air centrifugal compressors with a power of 455 HP each. Equipment sizing was calculated from the mass balance with a security factor of 1.2. The capital costs for each equipment was then calculated using the following expression (Eq. 2):

$$\text{Equipment Capital Costs} = x \times (CAP)^y \times (CEPCI_a/CEPCI_o) \qquad (2)$$

with x the equipment cost constant for the considered equipment estimated by regressing the equipment prices for different capacity.CAP stands for the desired capacity of the equipment and y is the scaling factor taken from the literature (Holland F.A. and J.K. Wilkinson, 1999; Remers D.S. and L.H. Chai, 1990; Ulrich G.D., 1984). $CEPCI_a$ is the actualized *Chemical Engineering Plant Cost Index* (568.3 in march 2013) and $CEPCI_o$ is the original CEPCI value (525.4) (Chemical Engineering, 2013). Energy requirements were also estimated based on the literature, or using supplier's data for specialised equipment. Labor requirements associated costs were calculated using factors from literature (Peters M.S. and K.D. Timmerhaus, 1991; Ulrich G.D., 1984). Finally indirect and general costs and the capital costs were included in the financial analysis. The major cost modeling parameters and monetary parameters used for the base case scenario are presented in Table 1. From a global point of view, all the model calculations are based on the capacity of the plant to treat rocks and not to treat the gaseous stream to sequester the carbon dioxide.

The profitability analysis was completed over a project lifetime of 10 years (See Table 3). The income tax rate was taken from the Canada Revenue Agency (2013) while the carbon credit price was based upon minimum value fixed by the Québec's law and in accordance with predicted values for the WCI cap and trade (Dumont, 2013; Gouvernement du Québec, 2013a). The magnesium carbonate sale price is a conservative value based on prices reported in 2000, where prices ranged from 200-350 US$/t (Kramer A.D., 2001). The same approach was chosen for the magnetic fraction price, based on the iron ore market in 2013 (Tuck C.A., 2013).

2.3 GHG balance

The GHG balance was calculated based on energy requirements and GHG emissions factors. Transportation emission factors were taken using the World Resource Institute, GHG protocol tool for mobile combustion Ver. 2.2 (2008). Emission factors for the in-plant energy use were taken from Natural Resource Canada (Office de l'éfficacité énérgétique, 2009).

3. Results

3.1 Global costs and sensitivity analysis

The global process cost data are presented in Table 2. A total of four different scenarios were used for this study corresponding to the two different modes for transportation of the rocks from the mine site to the emissions source (truck or train) and to the two different energy sources for thermal activation (natural gas or biomass). The others energy requirements for the equipment are furnished by electricity. Base case global processing costs ranged from 129 to 97 \$/t CO_2 sequestered. The impact of the type of transportation mode and the type of energy is clearly shown by these results.

A deeper regard on the parameters impacting the global costs is given by a sensitivity analysis for the four different scenarios. The results of this analysis for the NG/Truck option is given in Fig 3, but the other three scenarios gave comparable results. As also noted by Hitch and Dipple (2012), the sequestration efficiency has the most impact on the total global costs. This is clearly understandable because in this study, the amount of CO_2 treated directly impacts on the amount of solid required. Thus, a lower efficiency implies a larger quantity of rock that must be handled. In the case of 100% sequestration efficiency, global costs reduce to between 67 and 89 \$/t CO_2 sequestered. The distance and the mode of rock transportation also has a significant impact on the global process costs; as does the cost of natural gas or biomass, used in this study for the heat treatment of the serpentinite. This part represents the most important energy requirement of the process. The first heat activation required 317.5 kWh/t and the second one 268.0 kWh/t when considering an energy efficiency of 80%.The other energy requirements of the process are supplied with electricity. Milling of the residue to the desired particle size is also a significant energy requirement as the amount of energy required for the two milling step was estimated at 28.4 kWh/t. of residue, representing a cost of 1.00 US\$/t of residue. On the other hand the flue gas preconditioning required 10.6 kWh/t of residue for the compression giving a cost of 0.37 US\$/t.

Variation of the process costs as a function of the plant treatment capacity is presented in Fig. 4. Below a capacity of 50 t rocks/h, these costs increase significantly, whereas above this value, the economies of scale are less significant. Fig. 4 again illustrates that the use of biomass and train is the best option in terms of global process costs.

3.2 Profitability analysis

For all four scenarios, the capital cost of the plant was evaluated at 183 M$. The NPV ranged between 124 and 236 M$, with an IRR of between 25 and 37% (Table 2). The profitability analysis clearly shows that the implementation of a flue gas treatment plant using mineral carbonation is economically viable (Table 2). However, this profitability relies critically upon by-product generation. Without this additional income, the NPV value would range from -593 to -783 M$. As mentioned by Hitch and Dipple (2012) who based their profitability analysis on carbon credit prices, such income is very important in determining the feasibility of such an installation. The major advantage of the process studied here is the fact that two by-products a market value. Base case results showed values using very conservative incomes sale prices. Therefore, it is important to consider that NPV values in the reality would be higher. In addition, the payback period presented for the different scenario stay below 5 years.

3.3 GHG balance

While the economic feasibility of an environmental process is significant, its direct impact on the environment is considerable. In order to verify the integrity of the CO_2 sequestration process, the GHG balance was determined. The impact of solid transportation and the energy requirements for the process was used to calculate the total fuel and energy consumption and thus to evaluate the CO_2 equivalent emissions generated by the process. A breakdown of the emissions for each step is presented in the Fig. 5. The most significant GHG emissions of the process arise from the transport by truck and the heat activation of the residues when using natural gas. While natural gas has a lower emissions factor than coal or oil, it nevertheless emits 206 g CO_2 eq/kWh. The two heat activation steps required by the process, a total of 590 kWh per tonne of residue treated, thus results in 122 g CO_2 eq/ton of residue treated emission. Nevertheless, these emissions could be reduced, by increasing the first heat treatment efficiency and to look for another solution for the material reactivation layer in order to avoid the need of a second heat activation step. The sequestration of these emissions by a process using for example the industrial wastes generated by the emissions source, such as cement kiln dust could also be considered. Truck transportation presents an emission factor almost two times greater than train (0.12 vs 0.07). Carrying the solid material from the mining site to the industrial emitter using trucks represents a total of 35 kg CO_2 eq/tons of residue treated (for a distance of 171 km). The residue milling energy consumption were estimated at 19.5 kWh/tons of residue treated, which is in accordance compared with calculations made by McNab et al. (2009) for magnetite iron ore grinding, given that serpentinite hardness is less than magnetite. Thus particle reduction only represents a total emission of 0.04 kg CO_2/tons of residue treated because it is powered by electricity, whose emission factor is equal to 2 g CO_2 eq/kWh in Québec (Environnement Canada, 2011). This low emissions factor reflects the high dependence in Quebec on hydroelectric power. The emissions would be significantly larger in other areas of the world where electricity is generated from fossil fuels. The others steps of the process represent negligible sources of GHG.

The impact of the emissions on the overall CO_2 sequestration is mostly affected by the transportation and the energy requirements for the electrical equipment. Depending upon the type of transportation, these represent 44 and 35% of the total CO_2 sequestered by the process for when using natural gas with truck and train transportation respectively. When biomass is used, the impact of the emissions generated by the process is reduced to 9 and 1% for truck and train transportation respectively. The impact of the CO_2 avoidance ratio on the net global process cost is thus significant but such cost is still compensated by the by products sales incomes (Table 2).

4. Discussion and conclusion

The economic feasibility of a mineral carbonation process for post combustion CO_2 sequestration has been evaluated. The work has highlighted the importance of the CO_2 sequestration efficiency, as the global process costs are driven by the quantity of source rock required. Transportation of the solid feedstock is another sensitive parameter for the process costs. Although train represent a cheaper way to convey the reactive material to the industrial site, such a solution could impact on the capital costs, as some investment may be required to build loading and unloading facilities or to restore idle train routes. The distance between the emitters and the tailings is also a sensitive parameter, but the geographic situation of the solid feedstock within 200 km of an industrial emissions source reduces this impact.

Mining residues of the southern Quebec province are mostly composed of serpentinite. As described in the literature, the heat activation of the material is required in order to increase material sequestration efficiencies. In addition, in order to reduce limitations due to the formation of a passivation layer on the solid surface, a second heat treatment of the material was necessary. The energy requirements of the duplicate heat activation represent a major drawback for profitability and further research should be directed to improving the efficiency of the initial activation, so that the second can be eliminated. Heat integration of this step with the industrial process at the sequestration site should also be considered. The opportunity to use locally sourced biomass for this process step is more hypothetical, as considerable amounts of biomass would be required. Nevertheless, the use of a mixed energy source is possible.

This study confirmed the weaknesses of mineral carbonation already described in the literature (Huijgen et al., 2007), but also showed the economic feasibility for the process presented here. The precipitation of pure magnesium carbonates in a downstream process is novel and enhances the economic feasibility. In addition, the reuse of mining residues could represent an important employment opportunity for regions where mining industry is on the decline. The process is currently being tested under pilot scale conditions on a cement plant and the results from this trial will drive this opportunity closer to commercialisation.

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Figures list

Fig. 1. Map of the southern Quebec province. Larger tailings sites, A) Thetford Mines and B) Asbestos are indicated with red markers. Major industrial emission sources are also shown, with yellow markers for cement plants, blue markers for lime plants, white markers for refineries and light blue for steel plants. Circular dotted lines stand for a 100km and 200km radius from the mining residues respectively - orange for Asbestos and white for Thetford Mines. (Image Landsat, Google Earth 2013)

Fig. 2. Process flow sheet presenting the major steps and the inputs and outputs.

Fig. 3. Sensitivity analysis results for each scenarios.

Fig. 4. Treatment capacity sensitivity analysis for each different scenarios.

Fig. 5. Greenhouse gases emissions balance. Repartition between the different process steps as function of the transportation mode and energy source.

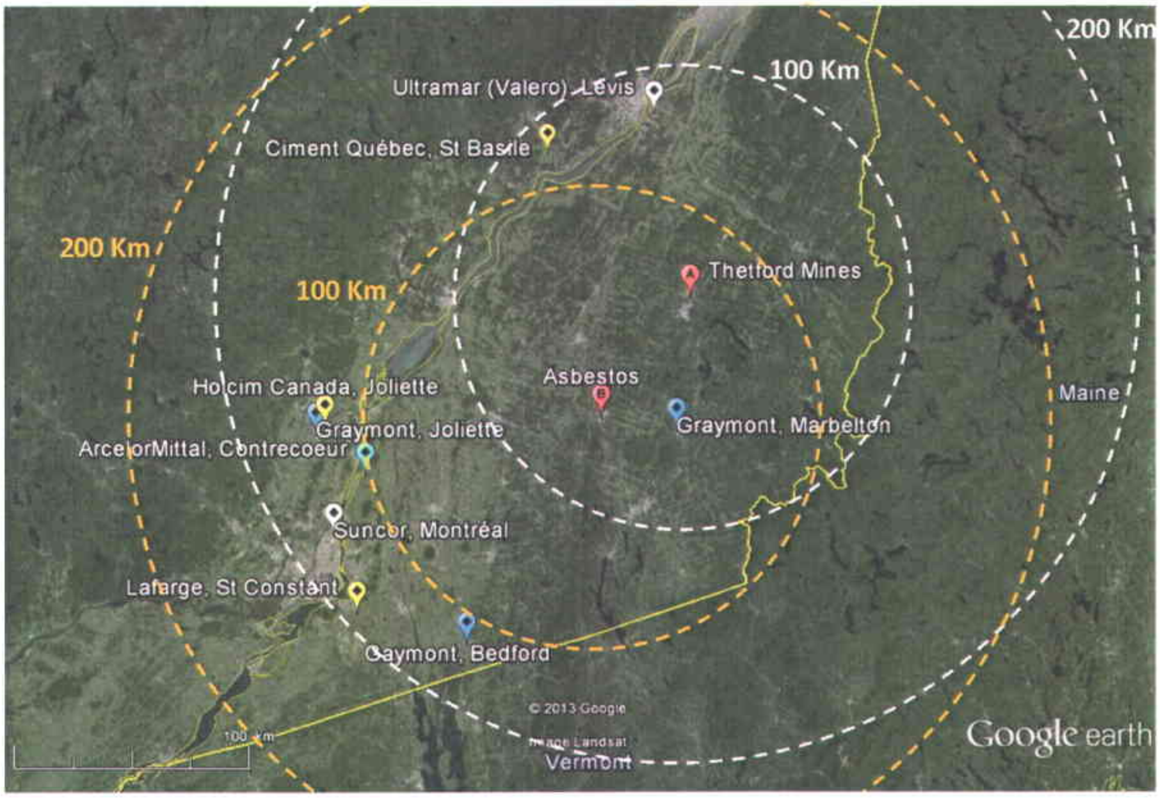

Fig.1. Map of the southern Quebec province. Larger tailings sites, A) Thetford Mines and B) Asbestos are indicated with red markers. Major industrial emission sources are also shown, with yellow markers for cement plants, blue markers for lime plants, white markers for refineries and light blue for steel plants. Circular dotted lines stand for a 100km and 200km radius from the mining residues respectively - orange for Asbestos and white for Thetford Mines. (Image Landsat, Google Earth 2013)

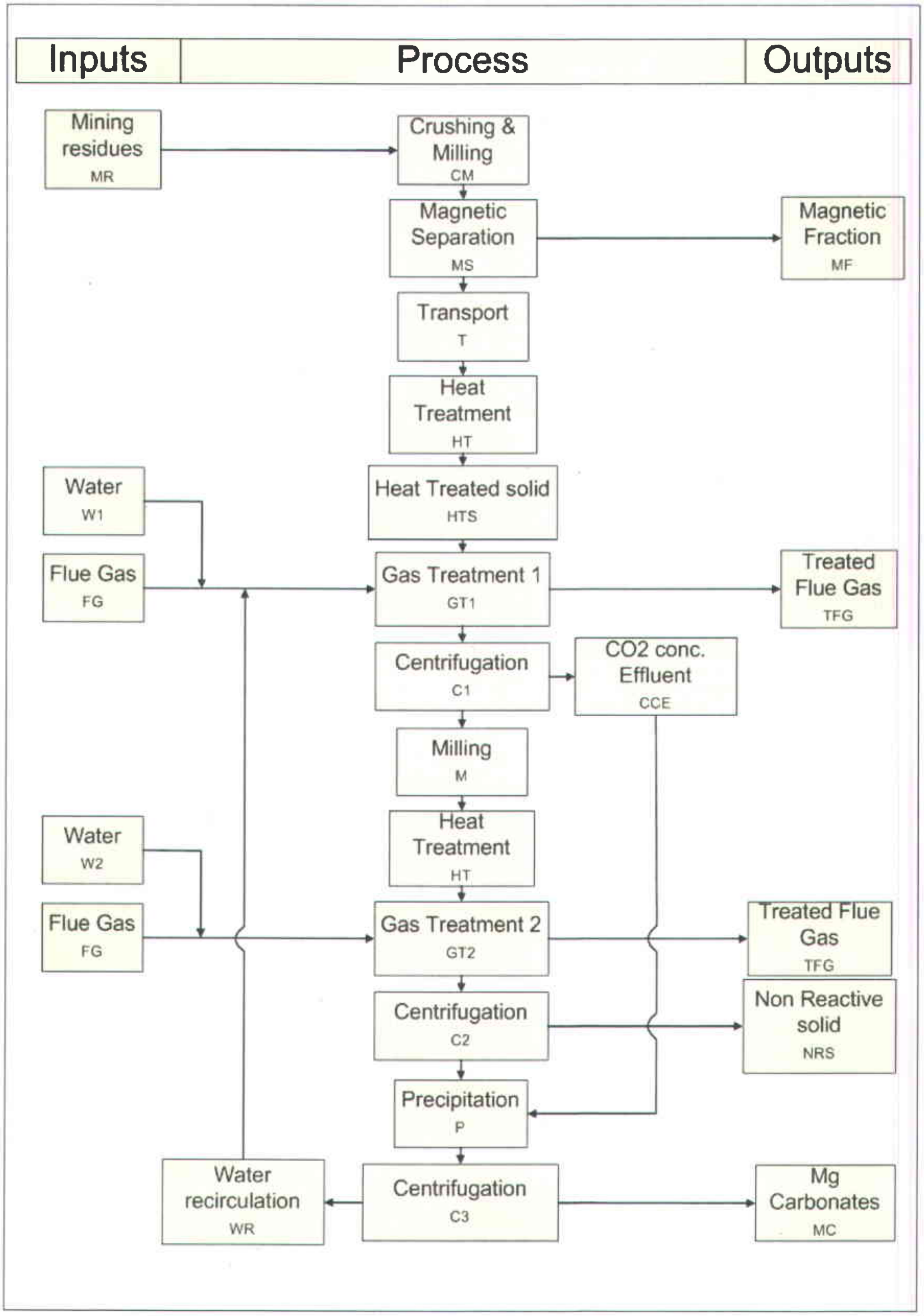

Fig. 2. **Process flow sheet presenting the major steps and the inputs and outputs.**

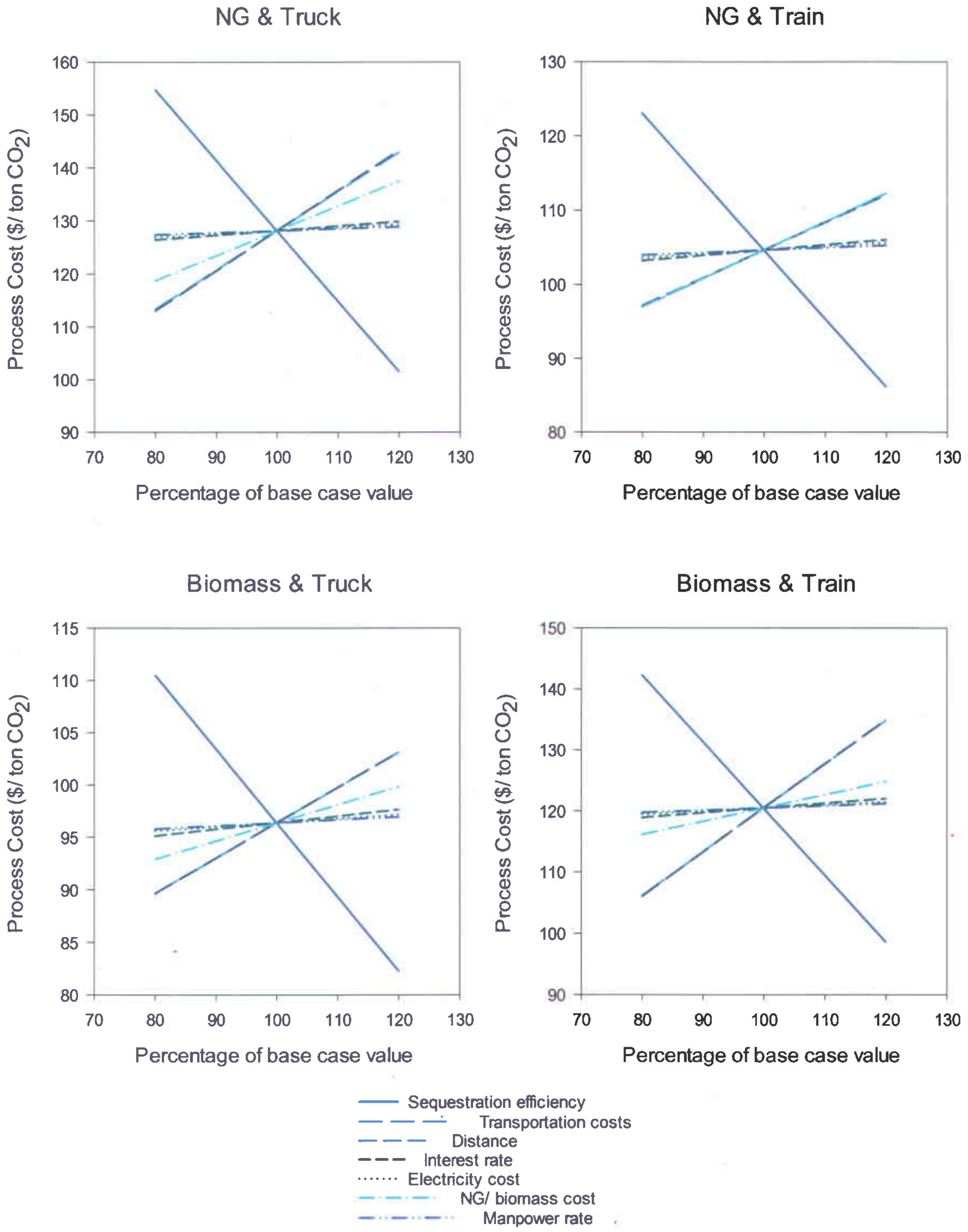

Fig. 3. **Sensitivity analysis results for each scenarios.**

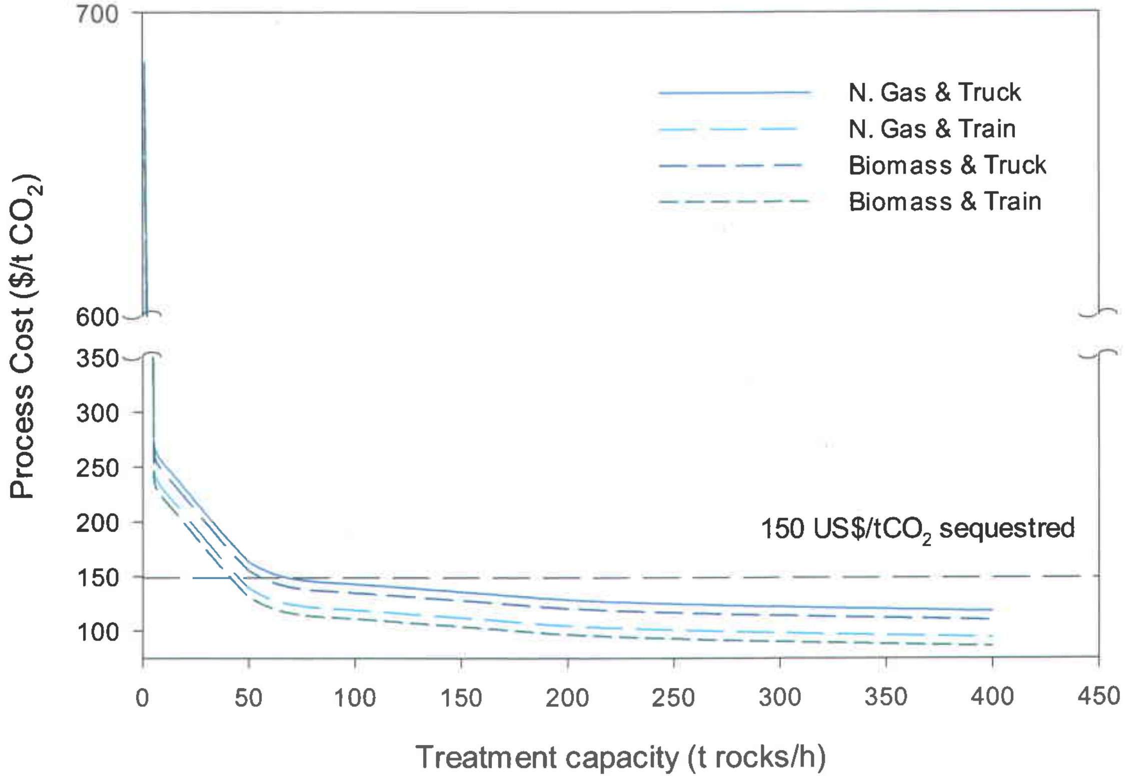

Fig. 4. **Treatment capacity sensitivity analysis for each different scenarios.**

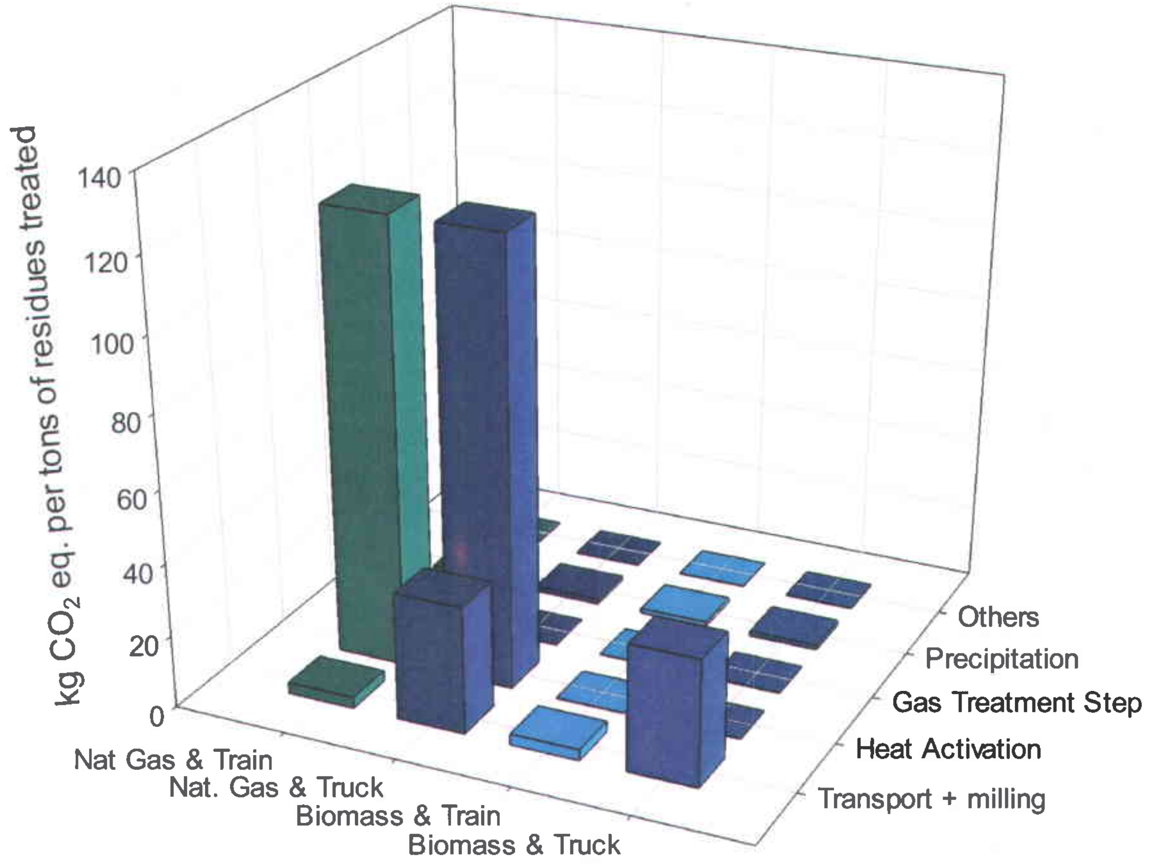

Fig. 5. Greenhouse gases emissions balance. Repartition between the different process steps as function of the transportation mode and energy source

Table 1

Base case input parameters for the profitability analysis

Input parameters	Unit	Base case Value
Cost model parameters:		
Plant treatment capacity	t rocks / h	200
Annual period of operation	Days	350
Daily period of operation	Hours	24
Annual Interest rate	%	2
Manpower rate	$ / h	25
Electricity unit cost	$ / kWh	0.035
Distance	Km	171
Sequestration efficiency	%	62
Energy unit cost	$ / MBtu	*Truck:* 3.00 *Train:* 1.54
Transportation unit cost	$ / km	*Truck:* 0.12 *Train:* 0.07
Profitability analysis parameters:		
Inflation rate	% / yr	2.0
Interest rate	% / yr	2.0
Discount rate	% / yr	8.0
Income tax	%	30
Carbon credit price	$ / tCO_2	20
Magnesium carbonate sale price	$ / t	100
Magnetic fraction sale price	$ / t	30

Table 2

Total process cost and profitability analysis for base case scenario.

Input parameters	Unit	Base case Value			
		Truck & NG (Tk&NG)	Train & NG (Tn&NG)	Truck & Biomass (Tk&B)	Train & Biomass (Tn&B)
Total process costs	$ / tCO$_2$	129	105	121	97
CO$_2$ avoidance ratio		0.56	0.65	0.91	0.99
Net total process cost	$ / tCO$_2$ avoided	230	162	133	97
Capital cost	$M	183			
NPV	$M	124	195	165	236
IRR	%	25	36	32	37
Payback period	yrs	4.7	3.5	4.1	3.4

CHAPITRE 5 : DEMANDE DE BREVET INTERNATIONAL

RESUME:

La présente invention concerne des processus, des procédés, un système et des utilisations en relation avec la séquestration chimique du dioxyde de carbone à partir d'un gaz contenant du dioxyde de carbone par carbonatation d'une substance contenant un métal alcalino-terreux. Le gaz contenant du dioxyde de carbone est mis en contact avec une bouillie aqueuse dans une unité de carbonatation pour la carbonatation d'au moins une partie du métal alcalino-terreux afin de produire un gaz appauvri en dioxyde de carbone et une bouillie chargée en carbonates qui est sensiblement dépourvue de carbonates de métal alcalino-terreux précipités. La bouillie chargée en carbonates est ensuite séparée en une phase aqueuse et une phase solide ; et la phase aqueuse est introduite dans une unité de précipitation pour précipiter les carbonates de métal alcalino-terreux. L'étape de carbonatation peut être réalisée à une température de carbonatation comprise entre environ 10 °C et environ 40 °C et à une pression de carbonatation comprise entre environ 1 bar et environ 20 bars. La phase solide peut être recyclée vers l'étape de carbonatation.

ABSTRACT:

Processes, methods, system and uses in relation to chemical sequestration of carbon dioxide from a carbon dioxide containing gas by carbonation of an alkaline earth metal containing material. The carbon dioxide containing gas is contacted with an aqueous slurry in a carbonation unit for carbonation of at least a portion of the alkaline earth metal to produce a carbon dioxide depleted gas and a carbonate loaded slurry which is substantially exempt of precipitated alkaline earth metal carbonates. The carbonate loaded slurry is then separated into an aqueous phase and a solid phase; and the aqueous phase is supplied to a precipitation unit for precipitating alkaline earth metal carbonates. The carbonation stage may be performed at a carbonation temperature between about 10° C and about 40° C and a carbonation pressure between about 1 bar and about 20 bars. The solid phase may be recycled to the carbonation stage.

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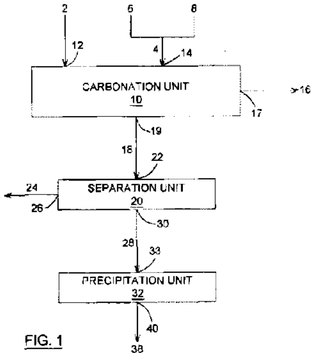

FIG. 1

(57) Abstract: Processes, methods, system and uses in relation to chemical sequestration of carbon dioxide from a carbon dioxide containing gas by carbonation of an alkaline earth metal containing material. The carbon dioxide containing gas is contacted with an aqueous slurry in a carbonation unit for carbonation of at least a portion of the alkaline earth metal to produce a carbon dioxide depleted gas and a carbonate loaded slurry which is substantially exempt of precipitated alkaline earth metal carbonates. The carbonate loaded slurry is then separated into an aqueous phase and a solid phase; and the aqueous phase is supplied to a precipitation unit for precipitating alkaline earth metal carbonates. The carbonation stage may be performed at a carbonation temperature between about 10° C and about 40° C and a carbonation pressure between about 1 bar and about 20 bars. The solid phase may be recycled to the carbonation stage.

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CARBON DIOXIDE CHEMICAL SEQUESTRATION FROM INDUSTRIAL EMISSIONS BY CARBONATION

FIELD OF THE INVENTION

The present invention relates to sequestration of carbon dioxide, and more particularly to chemical sequestration of carbon dioxide from industrial emissions by carbonation of an alkaline earth metal material.

BACKGROUND OF THE INVENTION

There are various methodologies that have been proposed for sequestering carbon dioxide.

Carbon dioxide is a greenhouse gas commonly contained in industrial emissions and it is desirable to sequester carbon dioxide gas in solid form.

In addition, there are various waste residues such as mining residue or waste concrete that are accumulated and not utilized for industrial processing.

Some background patent documents are as follows: US 7,604,787, US 7,731,921, US 7,815,880, US 7,919,064; US 8,105,558, US 8,114,374, US 2004/0131531, US 2007/022032, US 2007/0261947, US 2008/0112868, US 2008/0277319, US 2008/0299024, US 2010/0196235, US 2010/0221163, US 2011/0256048, US 2012/0177552, WO 2008/061305, WO 2009/092718.

Another previous report from the Albany Research Center, describes an ex situ industrial carbonation of serpentinite and describes it as an unviable option. 100% CO_2, critical high pressure and temperature, and pure mineral phases were used. [Gerdemann SJ, O'Connor WK, Dahlin DC, Penner LR and Rush H. (2007) *Ex situ* aqueous mineral carbonation. Environ. Sci. Technol. 41, 2587-2593] determines the cost of about $54 per ton of CO_2 (realizing no profit), which is a price derived from extraction of serpentinite, a costly high pressure mineralization process, and with no revalorisation of the magnesium carbonate.

There is indeed a need for a technology that overcomes at least some of the disadvantages of the carbon dioxide sequestration techniques that are known in the

field, and also that utilizes industrial emissions and alkaline earth metal containing residues.

SUMMARY OF THE INVENTION

The present invention provides various techniques related to the sequestration of carbon dioxide and the production of carbonate materials.

In one aspect, there is provided a process for sequestering carbon dioxide from a carbon dioxide containing gas. The process includes:

> contacting the carbon dioxide containing gas with an aqueous slurry including an alkaline earth metal containing material in a carbonation unit for carbonation of at least a portion of an alkaline earth metal to produce a carbon dioxide depleted gas and a carbonate loaded slurry including precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;
>
> removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into an aqueous phase including the precipitable carbonates and a solid phase; and
>
> supplying the aqueous phase to a precipitation unit and precipitating alkaline earth metal carbonates in the precipitation unit to produce a precipitation slurry.

In an optional aspect, the aqueous phase may include the precipitable carbonates and may be substantially exempt of precipitated alkaline earth metal carbonates.

In an optional aspect, the process may further include the step of agitating the aqueous slurry including an alkaline earth metal containing material during the step of contacting in the carbonation unit. Optionally, the process may also include the step of agitating the aqueous phase during the step of precipitating the alkaline earth metal carbonates in the precipitation unit.

In an optional aspect, the process *may further* include the step of mixing the alkaline earth metal containing material with water, prior to the step of contacting, to dissolve alkaline earth metal ions in aqueous phase and form the aqueous slurry.

In another optional aspect, the process may further include the step of mixing the alkaline earth metal containing material with water, simultaneously to the step of contacting, to dissolve alkaline earth metal ions in aqueous phase and form the aqueous slurry within the carbonation unit.

Optionally, the step of mixing may be performed so as to form the aqueous slurry having a mass concentration between 25 g/L and 300 g/L in grams of total solids per liter of aqueous slurry.

In an optional aspect, the process may further include separating the precipitation slurry into a solid stream including the alkaline earth metal carbonates and an aqueous stream.

In an optional aspect, the process may further include drying the solid stream including the alkaline earth metal carbonates.

In an optional aspect, the process may further include recycling at least a portion of the aqueous stream into the carbonation unit.

In an optional aspect, the process may further include recycling at least a portion of the solid phase into the carbonation unit as at least part of the alkaline earth metal containing material for contacting with the carbon dioxide containing gas.

In an optional aspect, the process may further include thermally pre-treating the alkaline earth metal containing material for dehydroxylation thereof, to produce a pre-treated alkaline metal earth containing material for contacting with the carbon dioxide containing gas. Optionally, the step of thermally pre-treating the alkaline earth metal containing material may include heating the alkaline metal earth containing material at a temperature between about 500℃ and about 800℃ dur ing a pre-treating time of about 10 minutes to about 60 minutes. Optionally, the temperature may be between about 600℃ and about 700℃ and the pre-treating time may be between about 15 minutes and about 40 minutes.

In an optional aspect, the process may further include crushing and/or grinding the alkaline metal earth containing material prior to the step of contacting with the carbon dioxide containing gas. Optionally, the step of crushing and/or grinding may be performed prior to the step of thermally pre-treating the alkaline earth metal containing material. Further optionally, the step of crushing and/or grinding may be performed to obtain solid particles having a median particle size between about 10 μm and about 45 μm and so as to obtain 90 % of the solid particles having a particle size between about 0 μm and about 75 μm.

In an optional aspect, the carbon dioxide containing gas may be derived from industrial emissions and may have a carbon dioxide concentration between 1% and 30%.

In an optional aspect, the process may further include controlling at least one of a carbonation temperature, an agitation speed and a carbonation pressure in the carbonation unit.

Optionally, the step of contacting in the carbonation unit may be performed at the carbonation temperature between about 10℃ and about 40℃. Optionally, the carbonation temperature may be between about 20℃ and about 30℃.

Optionally, the step of contacting in the carbonation unit may be performed at the carbonation pressure between about 1 bar and about 20 bars. Optionally, the carbonation pressure may be between about 2 bars and about 12 bars.

Optionally, the agitation speed in the carbonation unit may be between about 400 rpm and about 800 rpm, and further optionally between about 500 rpm and about 650 rpm.

In an optional aspect, the step of precipitating may be performed at a precipitation temperature between about 20℃ and about 80℃ for a precipitation time between about 0.5 hours and about 12 hours. Optionally, the step of precipitating may include agitating the aqueous phase.

In an optional aspect, the alkaline earth metal containing material may include at least one of sandstone, granite, anorthosite, basalt, serpentinite, peridotite, serpentinized peridotite, ophiolitic rocks, mafic and ultramafic rocks, rocks containing more than 10% of pyroxene and peridot, calcium silicate, magnesium silicate, feldspar, plagioclase feldspar, peridot, pyroxene, olivine, serpentine, wollastonite, calcium oxide, magnesium oxide, brucite, mafic and ultramafic minerals, steelmaking slag, steelmaking worn MgO brick, rotary kiln dust (CKD, LKD), waste cement, waste concrete, construction and demolition waste, concrete with aggregates, concrete brick, concrete, red brick, phyllosilicate mining residue and chrysotile mining residue.

In an optional aspect, the alkaline earth metal may include calcium or magnesium.

In an optional aspect, the process may further include supplying continuously the carbon dioxide containing gas to the carbonation unit. Optionally, the process may include controlling or managing a maximal quantity of dissolved carbon dioxide in the carbonate loaded slurry produced in the carbonation unit, the maximal quantity of dissolved carbon dioxide being chosen to reduce or avoid precipitation of the alkaline earth metal carbonates in the carbonation unit. Optionally, the maximal quantity of dissolved carbon dioxide may be at most 5 g/L.

In another optional aspect, the carbon dioxide containing gas may include a plurality of carbon dioxide containing gas portions, the process including:

> supplying at least one carbon dioxide containing gas portion to the carbonation unit;
>
> contacting the aqueous slurry with the at least one carbon dioxide containing gas portion in the carbonation unit for production of the carbonate loaded slurry;
>
> removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into the aqueous phase including the precipitable carbonates and the solid phase; and
>
> recycling the solid phase to the carbonation unit and supplying water to the carbonation unit to form a new portion of aqueous slurry;
>
> contacting the new portion of aqueous slurry with another carbon dioxide containing gas portion for production of the carbonate loaded slurry.

In an optional aspect, the carbon dioxide containing gas may be supplied to the carbonation unit as a plurality of carbon dioxide containing gas portions, the process including:

> contacting the aqueous slurry with at least one carbon dioxide containing gas portion in the carbonation unit for production of the carbonate loaded slurry;

removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into the aqueous phase including the precipitable carbonates and the solid phase; and

supplying the aqueous phase including the precipitable carbonates to the precipitation unit, precipitating the alkaline earth metal carbonates in the precipitation unit to produce the precipitation slurry and separating the precipitation slurry into a solid stream including the alkaline earth metal carbonates and an aqueous stream;

recycling the solid phase and the aqueous stream to the carbonation unit to produce a new portion of aqueous slurry and contacting the new portion of aqueous slurry with another carbon dioxide containing gas portion for production of the carbonate loaded slurry.

Optionally, the process may include supplying water to the carbonation unit as a make up stream of the new portion of aqueous slurry.

In an optional aspect, the step of contacting in the carbonation unit may be performed for a maximal gas contact time, the maximal gas contact time being controlled or managed to reduce or avoid precipitation of the alkaline earth metal carbonates in the carbonation unit. Optionally, the maximal gas contact time may be between about 1 minute and about 60 minutes.

In an optional aspect, the process may also include crushing and/or grinding the solid phase prior to the step of recycling to the carbonation unit to produce the new portion of aqueous slurry.

In another aspect, there is provided a process for sequestering carbon dioxide from a carbon dioxide containing gas. The process includes:

contacting the carbon dioxide containing gas with an aqueous slurry including a magnesium containing material in a carbonation unit at a carbonation temperature between about 10ºC and about 40ºC and a carbonation pressure between about 1 bar and about 20 bars, for carbonation of at least a portion of magnesium to produce a carbon dioxide depleted gas and a carbonate loaded slurry including precipitable carbonates and substantially exempt of precipitated magnesium carbonates.

In an optional aspect, the process may include:

removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into a solid phase and an aqueous phase including precipitable carbonates and substantially exempt of precipitated magnesium carbonates; and

supplying the aqueous phase to a precipitation unit and precipitating magnesium carbonates in the precipitation unit to produce a precipitation slurry including the precipitated magnesium carbonates.

In an optional aspect, the process may further include separating the precipitation slurry into a solid stream including the precipitated magnesium carbonates and an aqueous stream.

In another aspect, there is provided a process for sequestering carbon dioxide from a carbon dioxide containing gas, the process including contacting the carbon dioxide containing gas with an alkaline earth metal containing material in a substantially dry form in at least one carbonation unit at a carbonation temperature between about 200℃ and about 500℃ and a carbonation pressure between about 1 bar and about 20 bars, for carbonation thereof to produce carbonates and a carbon dioxide depleted gas.

In another aspect, there is provided a method for sequestering carbon dioxide from industrial emissions by contacting the industrial emissions with magnesium silicate material, in wet or dry form, to produce a carbon dioxide depleted gas and a carbonated magnesium silicate material.

In another aspect, there is provided a method for manufacturing alkaline earth metal carbonates, the method including:

a contacting stage wherein industrial emissions including carbon dioxide are contacted with an aqueous slurry including an alkaline earth metal containing material, to produce a carbon dioxide depleted gas and an alkaline earth metal carbonate stream substantially exempt of precipitated alkaline earth metal carbonates;

a precipitation stage wherein alkaline earth metal carbonates are precipitated from the alkaline earth metal carbonate stream, thereby producing a precipitation slurry; and

a separation stage wherein the precipitation slurry is separated into the precipitated alkaline earth metal carbonates and an aqueous phase.

In another aspect, there is provided a method for manufacturing alkaline earth metal carbonates, the method including:

a contacting stage wherein industrial emissions including carbon dioxide are contacted with an aqueous slurry including an alkaline earth metal containing material, to produce a carbon dioxide depleted gas and an alkaline earth metal carbonate stream including precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;

a first separation stage wherein the alkaline earth metal carbonate stream is separated into a solid phase and an aqueous phase including the precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;

a recycling stage wherein the solid phase is recycled to the carbonation stage as at least a portion of the alkaline earth metal containing material;

a precipitation stage wherein alkaline earth metal carbonates are precipitated from the aqueous phase, thereby producing a precipitation slurry including the precipitated alkaline earth metal carbonates; and

a separation stage wherein the precipitation slurry is separated into the precipitated alkaline earth metal carbonates and an aqueous phase.

In another aspect, there is provided a carbon dioxide sequestration system for sequestering carbon dioxide from a carbon dioxide containing gas. The system includes:

at least one carbonation unit having:

a gas inlet for receiving the carbon dioxide containing gas,

a slurry inlet for receiving an aqueous slurry including an alkaline earth metal containing material,

a carbonation vessel for the carbonation of at least a portion of an alkaline earth metal of the aqueous slurry with carbon dioxide to produce a carbon dioxide depleted gas and a carbonate loaded slurry including precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates,

a slurry outlet for releasing the carbonate loaded slurry including precipitable carbonates, and

a gas outlet for releasing the carbon dioxide depleted gas;

a separation unit having:

a slurry inlet for receiving the carbonate loaded slurry including precipitable carbonates from the slurry outlet of the at least one carbonation unit,

a separation chamber for separation of the carbonate loaded slurry including precipitable carbonates into a solid phase and an aqueous phase including the precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates,

a liquid outlet for releasing the aqueous phase, and

a solid outlet for releasing the solid phase; and

a precipitation unit having:

a slurry inlet for receiving the aqueous phase including the precipitable carbonates from the liquid outlet of the separation unit,

a precipitation chamber for precipitation of the alkaline earth metal carbonates and formation of a precipitation slurry, and a liquid outlet for releasing the precipitation slurry.

In another aspect, there is provided a use of a magnesium containing material in the form of an aqueous slurry to contact and sequestrate carbon dioxide from a carbon dioxide containing gas at a temperature between about 20℃ and about 30℃ and a pressure between about 2 bars and about 12 bars to form magnesium carbonates.

In another aspect, there is provided a use of a phyllosilicate mining residue to sequestrate carbon dioxide from industrial emissions and produce magnesium carbonates. Optionally, the phyllosilicate mining residue includes at least one of lizardite, antigorite, brucite, iron oxide, chromium oxide and chrysotile.

In another aspect, there is provided a precipitated calcium or magnesium carbonate (PCC or PMC) produced by contacting a calcium or magnesium containing material in wet form with carbon dioxide from industrial emissions in a carbonation unit to form a carbonate loaded slurry, and precipitating the calcium or magnesium carbonate from the carbonate loaded slurry in a precipitation unit.

In another aspect, there is provided a precipitated calcium or magnesium carbonate (PCC or PMC) including at least 95 wt% of calcium or magnesium carbonate in dry form or hydrated form.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments, aspects and implementations of the present invention are represented in and will be further understood in connection with the following figures.

Fig 1 is a process flow diagram of wet carbonation according to an optional aspect of the present invention.

Fig 2 is a schematic of carbonation unit according to an optional aspect of the present invention.

Fig 3 is a process flow diagram of wet carbonation according to an optional aspect of the present invention.

Fig 4 is a schematic of process steps for wet carbonation with a recirculation scenario according to an optional aspect of the present invention.

Fig 5 is a solubilised magnesium quantity vs temperature graph for wet carbonation with three different reaction times according to an optional aspect of the present invention.

Fig 6 is a solubilised magnesium quantity vs temperature graph for wet carbonation of an aqueous slurry with three different pulp densities according to an optional aspect of the present invention.

Fig 7 is a CO_2 removal vs gas/liquid ratio (GLR) graph for wet carbonation of an aqueous slurry of various pulp densities according to an optional aspect of the present invention.

Fig 8 is a CO_2 removal vs time graph for wet carbonation according to an optional aspect of the present invention.

Fig 9 is a CO_2 flow vs time graph for wet carbonation in continuous mode showing CO_2 removal efficiency at 3.4 bars and 42 mL/min according to an optional aspect of the present invention.

Fig 10 is a response surface graph showing the interaction of temperature and pressure on CO_2 removal percentage in direct dry gas solid carbonation.

Fig 11 is a pressure versus time graph of gas/solid carbonation at a temperature of 258°C, and a pressure of 5.6 atm over 10 minutes according to an optional aspect of the present invention.

While the invention will be described in conjunction with example embodiments, it will be understood that it is not intended to limit the scope of the invention to these embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included as defined by the appended claims.

DETAILED DESCRIPTION

Various techniques are described herein for sequestering carbon dioxide and producing alkaline earth metal carbonates.

In one aspect, there is provided a process for chemically sequestering carbon dioxide from a carbon dioxide containing gas by producing alkaline earth metal carbonates. The carbon dioxide containing gas may be issued from industrial emissions and have various carbon dioxide concentrations according to the industrial process from which the emissions are derived.

In some optional aspects, there is provided a process for carbon dioxide chemical sequestration from industrial emissions that contain carbon dioxide by carbonation using magnesium or calcium silicate.

Much of the research up to this juncture has been performed using gases containing 100% CO_2, which implies that carbon dioxide from the chimney of an industrial facility must first be concentrated using separate technologies before it can be treated using carbonation. This implies a more costly process. In 2011, a carbon capture and sequestration (CCS) pilot plant opened at a coal fired facility in the United Kingdom. Experts have estimated that 16% to 40% of the energy produced could end up being used to capture and store carbon. This corresponds to a 100 million dollar producing electricity plant to a cost between 16 to 40 million dollars.

Embodiments of the present invention may enable increasing the economic viability by providing profit or a cost between zero to 10% of the value of the produced energy.

In some optional aspects, the carbon dioxide containing gas may advantageously be gas emissions that are directly used as they are produced from a plant. For example, for a cement factory, one may use a gas containing 18.2% CO_2, 4.11% O_2 and 77.69% N_2. Optionally, the carbon dioxide containing gas derived from industrial emissions may have a carbon dioxide concentration between about 1% and about 30%.

Embodiments of the present invention may also enable to produce valuable alkaline earth metal carbonates from an alkaline earth metal containing material.

It should be understood that the alkaline earth metal containing material may be a natural material that may include but is not limited to alkaline earth metal containing minerals and alkaline earth metal containing rocks. For example, the alkaline earth metal containing material may include serpentine or serpentinite. Optionally, the alkaline earth metal containing material may include alkaline earth metal containing rocks such as sandstone, granite, anorthosite, basalt, serpentinite, peridotite, serpentinized peridotite, ophiolitic rocks, mafic and ultramafic rocks (containing Mg and Fe minerals), rocks containing more than 10% of pyroxene and peridot, or a combination thereof. Optionally, the alkaline earth metal containing material may also include a phyllosilicate. Further optionally, the alkaline earth metal containing material may include alkaline earth metal containing minerals such as calcium silicate, magnesium silicate, feldspar, plagioclase feldspar (andesine), peridot (olivine sand), pyroxene (enstatite olivine sand), olivine, serpentine (as in mineral family containing antigorite, chrysotile, lizardite), wollastonite, calcium oxide (CaO), magnesium oxide or periclase (MgO), brucite ($Mg(OH)_2$), mafic and ultramafic minerals (containing Mg and Fe), or a combination thereof.

The alkaline earth metal containing material may also be issued from various industrial wastes or residues such as slag, cement waste, mining processing waste and mineral processing waste, which are available without the need to be mined from geological formations. Optionally, the slag may include steelmaking slag, steelmaking worn MgO brick or a combination thereof. Optionally, the cement waste may include rotary kiln dust (CKD, LKD), waste cement, waste concrete, construction and demolition waste, concrete with aggregates, concrete brick, concrete, red brick or a combination thereof. Optionally, the mining and mineral processing waste may include phyllosilicate mining residue, chrysotile mining residue, serpentine (as in the rock matrix containing the ore) or a combination thereof.

Therefore, embodiments of the present invention may further benefit from additional advantages regarding the efficiency and cost of the process.

Referring to Fig 1, in some implementations, the process includes the step of supplying the carbon dioxide containing gas 2 and an aqueous slurry 4 including an alkaline earth metal containing material 6 and water 8 to a carbonation unit 10. The carbonation unit 10 may include a gas inlet 12 for receiving the carbon dioxide containing gas 2 and a slurry inlet 14 for receiving the aqueous slurry 4. The process then includes the step of contacting the carbon dioxide containing gas 2 and the aqueous slurry 4 in the carbonation unit 10, for carbonation of at least a portion of the alkaline earth metal. A carbon dioxide depleted gas 16 and a carbonate partially loaded slurry 18 including precipitable carbonates are produced. The process may also include the step of removing the carbon dioxide depleted gas 16 from the carbonation unit 10 through a gas outlet 17, and the carbonate loaded slurry 18 through a slurry outlet 19. In some implementations, the carbonate loaded slurry contains substantially no precipitated carbonates within and as it is released from the carbonation unit 10. The carbonate loaded slurry 18 is then separated in a separation unit 20 into a solid phase 24 and an aqueous phase 28 including the precipitable carbonates, which are respectively released from the separation unit 20 via a solid outlet 26 and a liquid outlet 30. In some implementations, the aqueous phase 28 contains substantially no precipitated carbonates within and as it is released from the separation unit 20. The aqueous phase 28 may be then supplied to a precipitation unit 32 via a liquid inlet 33. The process may include precipitating at least a portion of the precipitable carbonates of the aqueous phase 28 into alkaline earth metal carbonates in the precipitation unit 32, thereby producing a precipitation slurry 38 including the alkaline earth metal carbonates which is released from the precipitation unit 32 via a slurry outlet 40.

It should be understood that the aqueous slurry 4 including the alkaline earth metal containing material 6 may be formed prior to being supplied to the carbonation unit 10 as seen in Fig 2, but may also be directly formed in the carbonation unit 10 by supplying separately the alkaline earth metal containing material 6 and water 8 to the carbonation unit 10.

In some optional aspects, the process may further include the step of agitating the aqueous slurry in the carbonation unit to enhance contact between the carbon dioxide containing gas and the alkaline earth metal containing material. The agitation may be ensured by a mechanical agitator such as a propeller having an agitation speed between about 400 rpm and about 800 rpm, optionally between about 500 rpm and about 650 rpm. It should be understood that the agitation step is not limited to a mechanical agitation and may include various known and suitable agitation techniques such as gas fluidisation.

In other optional aspects, the process may also include agitating the aqueous phase in the precipitation unit to enhance precipitation of the alkaline earth metal carbonates.

In some optional aspects, the alkaline earth metal containing material may be mixed with water so as to obtain the aqueous slurry having a pulp density (also referred to as mass concentration of total solids per liter of slurry) between 25 g/L and 300 g/L. A low pulp density may favor the dissolution of the alkaline earth metal in the aqueous slurry. The influence of the density of the aqueous slurry on carbon dioxide removal efficiency is shown in Example 2.

In some optional aspects, the process may include thermally pre-treating the alkaline earth containing material to perform dehydroxylation. The alkaline earth containing material may indeed include undesirable water which is at least partially removed with the thermal pre-treatment. During the thermal pre-treatement, water is vaporized and the crystalline structure of the alkaline earth metal containing material may be changed into a more chemically active structure, allowing better dissolution of the alkaline earth metal in aqueous phase. Optionally, the process may include heating the alkaline earth metal containing material at a pre-treating temperature between about 500℃ and about 800℃ during a pre-treating time between about 10 minutes and about 60 minutes. Optionally, the pre-treating temperature may be between about 600℃ and about 700℃ and the pre-treating time may be between about 15 minutes and about 40 minutes. Optionally, the pre-treating temperature may be sufficiently low to avoid recrystallization of the alkaline earth metal containing material. The influence of the thermal pre-treatment on carbon dioxide removal efficiency is shown in Example 3.

In some optional aspects, the process may include crushing and/or grinding the alkaline earth metal containing material to enhance the available surface for contact with the carbon dioxide containing gas and favor carbonation of the alkaline earth metal. Optionally, the alkaline earth metal containing material may be crushed and/or grinded such that the average size of the material particles is between about 10 µm and about 45 µm and such that at least about 90 % of the solid particles having a particle size between about 0 µm and about 75 µm. Optionally, the crushing and/or grinding step may be performed before the thermal pre-treating step as the dehydroxylation may be favored by using material particles of reduced size.

Referring to Fig 3, the process may include crushing and/or grinding the alkaline earth metal containing material 6 in a crushing/grinding unit 42 so as to reduce the size of the alkaline earth metal containing material particles. The crushed and/or grinded material 6 is then supplied to a thermal pre-treatment unit 44 for dehydroxylation thereof as mentioned above. The water 8 and the pre-treated material 6 may be supplied to the carbonation unit 10 separately so as to form the aqueous slurry within the carbonation unit 10 for contact with the supplied carbon dioxide containing gas 2 to produce the aqueous slurry 18 including precipitable carbonates and the carbon dioxide depleted gas 16. The aqueous slurry 18 is supplied to the separation unit 20 for separation thereof into the aqueous phase 28 including precipitable carbonates and the solid phase 24. At least a portion 25 of the solid phase 24 may be recycled as at least a part of the alkaline earth metal material 6 to the crushing/grinding unit 42. At least part of the aqueous phase 28 including the precipitable carbonates is supplied to the precipitation unit 32 for precipitation of the alkaline earth metal carbonates and production of the precipitation slurry 38. The precipitation slurry 38 may be supplied to a second separation unit 46 for separation into the alkaline earth metal carbonates stream 50 and a liquid stream 48. At least a portion of the liquid stream 48 may be recycled as at least a portion of the water 8 to the *carbonation unit* 10.

In some optional aspects, the step of precipitating the alkaline earth metal carbonates may be performed at a precipitation temperature between about 20℃ and about 80℃, and a precipitation time between about 0.5 hours and about 12 hours with or without agitation.

In some optional aspects, the precipitates of alkaline earth metal carbonates produced according to the present process have a purity between 90 and 99.9%.

In some optional aspects, the carbon dioxide containing gas may be supplied continuously to the carbonation unit while keeping a certain or desired carbon dioxide removal *efficiency (see* Example 5). Optionally, the process may be operated according to a series of batch operations including recycling streams so as to increase the solid material carbonation rate (see Example 6). For example, a recirculation process scenario may be performed such that a same portion of alkaline earth material would contact several portions of carbon dioxide containing gas before precipitation into alkaline earth metal carbonates.

In some optional aspects, the process may include recycling the solid phase separated from the carbonate loaded slurry to produce a new portion of aqueous slurry for contacting with the carbon dioxide containing gas in the carbonation unit. It should be noted that recycling may also be referred to herein as recirculating.

Fig 4 shows a process diagram schematic of the various steps associated with recirculation of various liquid and solid streams according to optional embodiments of the present invention. A plurality of streams may indeed be recycled to the carbonation unit while the carbon dioxide containing gas is supplied continuously or in batch mode to the carbonation unit.

Batch mode gas supply

In some optional aspects, the carbon dioxide containing gas may be supplied to the carbonation unit via carbon dioxide containing gas portions.

Step 1:

A first portion of carbon dioxide containing gas, referred to as "Gas 1", is contacted in the carbonation unit during a specific time by an aqueous slurry, resulting from the combination of "Solid 1" and "Liquid". For example, the aqueous slurry may have a mass concentration in alkaline earth metal containing material of 150 g/L, and the aqueous slurry may be contacting each carbon dioxide containing gas portion during 30 minutes.

After each contacting step of 30 minutes, the produced carbonate loaded slurry is separated into a solid phase and an aqueous phase. It should be noted that the first portion of gas "Gas 1" may be provided as two sub-portions for example so as to comply with pressure limits. Two sub-portions of gas, each contacting the solid for 15 minutes, may therefore be provided successively in the carbonation unit.

A mass balance between the carbon dioxide containing gas and the carbon dioxide depleted gas showed that a maximum of 5.91 g CO_2/L of gas (1.64 g C/L of gas) was treated after each contact step of 30 minutes.

Step 2:

The aqueous phase is then supplied to the precipitation unit and once the alkaline earth metal carbonates have sufficiently precipitated, the precipitation slurry is separated into a solid stream and an aqueous stream.

Step 3:

The aqueous stream is then recycled as "Liquid" into the carbonation unit.

The three above mentioned steps 1 to 3 are repeated two more times for contacting second and third portions of carbon dioxide containing gas, referred to as "Gas 2" and "Gas 3".

After contacting with "Gas 2" and "Gas 3", the solid phase "Solid 1" is dried, grinded and heated in the pre-treatment unit as previously described.

Steps 1 to 3 are performed three more times with the grinded and heated solid phase "Solid 1" to contact successively "Gas 4", "Gas 5" and "Gas 6". After having contacted six carbon dioxide containing gas portions ("Gas 1" to "Gas 6"), the solid phase reaches its reactivity limits.

All the process steps described above may then be repeated with a new portion of alkaline earth metal containing material.

Continuous mode gas supply

In some other optional aspects, the carbon dioxide containing gas flow may be supplied continuously to the carbonation unit. In batch mode, the key parameter to be controlled was the contact time of a portion of carbon dioxide containing gas. Alternatively, in continuous mode, the key parameter to be controlled is the quantity of dissolved carbon dioxide in the aqueous slurry.

According to the above example of batch mode operation, a maximum of 5.91 g CO_2/L of gas (1.64 g C/L of gas) was treated after each contact step of 30 minutes. Considering that all of the treated carbon dioxide is dissolved into the aqueous slurry, the maximum concentration of dissolved carbon dioxide should not exceed about 5.0 g C/L. Above this value, precipitation within the reactor may occur.

Therefore, in continuous mode, once a concentration of dissolved carbon dioxide of 5.0 g C/L is measured in the aqueous slurry, the aqueous slurry is removed from the carbonation unit and separated into the solid phase and the aqueous phase. The aqueous phase is then supplied to the precipitation unit.

Optionally, depending on the precipitation rate of the alkaline earth metal carbonates in the precipitation unit, a certain volume of water could be supplied to the aqueous phase in order to maintain a low dissolved carbon dioxide concentration in the recirculated aqueous phase along the steps.

For example, once the cumulative quantity of treated carbon dioxide has reached 16.04 g CO_2/L of gas (4.4 g C/L of gas), the separated solid phase may be dried, grinded and heated before further recycling.

Steps 1 to 3 may therefore be performed again successively following the same scenario as described above, in order to reach a cumulative amount of treated carbon dioxide of about 27.28 g CO_2/L of gas (7.47 g C/L of gas) for the overall series of three steps 1 to 3. Then, a new portion of alkaline earth metal containing solid may be used.

It should be understood that any one of the above mentioned aspects of each process, method, system, use and material may be combined with any other of the aspects thereof, unless two aspects clearly cannot be combined due to their mutually exclusivity. For example, the various operational steps of the processes described herein-above, herein-below and/or in the appended figures, may be combined with any of the method, system or use descriptions appearing herein and/or in accordance with the appended claims.

It should also be understood that various parameter values obtained and/or described in any of the examples, tables and description herein may be considered as maximal, minimal or intermediate values, and that various ranges may be derived from these maximal, minimal or intermediate values as described herein or in the appended figures and claims.

EXAMPLES

EXAMPLE 1 : Wet carbonation of chrysotile mining residues

A first series of experiments were carried out, using chrysotile mining residues composed of lizardite, antigorite, brucite, iron oxides, chromium oxides and a low content of chrysotile, to optimize conditions for the wet carbonation on sample size of around 7 g with grain size inferior to 75 µm and a pulp density of 15% (a mass of 150 g of solid per liter of liquid). The temperature and reaction duration were kept stable at 25°C and 6 h respectively. The variable parameters are pressure, NaCl and $NaHCO_3$

content and heat treated sample or not. They were optimized on the basis of percentage of CO_2 removal and the percentage of solid carbonate formed (dependent variables). The various conditions and results obtained are given in Table 1.

From this table, it appears that a removal of CO_2 up to 87% can be achieved for a pressure of 10.2 atm and heat treated sample. CO_2 removal seems independent from NaCl content and slightly dependent to $NaHCO_3$ content in the solution, while thermal pre-treatment is necessary. On a run of 6 h, in these conditions, 24% of the sample had been carbonated.

Table 1 **Box-Benkhen matrix for the first set of assays and results (T = 25°C, t = 6 h)**

Run	Pressure (atm)	NaCl (M)	$NaHCO_3$ (M)	Thermal Pre-treatment	CO_2 removal (%)	Carbonate solid formation (%)
1	45.9	0.5	0.32	Yes	30	0
2	10.2	0.5	0.64	Yes	78	5.43
3	10.2	1	0.32	No	49	2.24
4	10.2	0.5	0	Yes	79	19.13
5	45.9	1	0	No	21	0
6	45.9	0.5	0.32	No	27	0.4
7	81.7	1	0.32	No	23	0.16
8	81.7	0.5	0.64	No	10	0.91
9	10.2	0	0.32	No	44	0.72
10	45.9	0.5	0.32	No	15	0.4
11	81.7	1	0.32	Yes	31	0.19

12	45.9	0.5	0.32	Yes	35	0.66
13	45.9	0	0	Yes	28	0
14	45.9	0.5	0.32	No	15	0.68
15	45.9	0.5	0.32	No	13	0.33
16	45.9	1	0.64	No	19	0.87
17	45.9	0.5	0.32	Yes	45	0
18	10.2	1	0.32	Yes	84	37.06
19	45.9	1	0.64	Yes	31	1.22
20	45.9	1	0	Yes	29	0
21	45.9	0	0.64	No	20	0.88
22	45.9	0.5	0.32	No	31	0.52
23	10.2	0.5	0	No	46	0
24	81.7	0	0.32	Yes	32	1.21
25	45.9	0.5	0.32	Yes	32	0.36
26	10.2	0.5	0.64	No	42	2.88
27	45.9	0	0.64	Yes	38	0.6
28	81.7	0	0.32	No	13	0.57
29	81.7	0.5	0	Yes	32	0
30	81.7	0.5	0.64	Yes	37	1.25
31	45.9	0.5	0.32	Yes	36	0

32	**45.9**	**0**	**0**	**No**	**20**	**0**
33	**81.7**	**0.5**	**0**	**No**	**10**	**0**
34	**10.2**	**0**	**0.32**	**Yes**	**87**	**40.01**

The time duration of 6 h for carbonation in optimized conditions was very long, carbonation assays were carried out for shorter reaction time to verify the time dependency of the rate of wet carbonation. The experiments conditions and results are presented in Table 2. Temperature is kept constant at 25°C and pulp density is kept constant at 15%.

Table 2 **Experimental conditions and results for wet carbonation of heat treated sample for 30 min duration**

	Input					
	Time (min)	Volume Liq. (mL)	Weight Spl. (g)	Pressure (atm)	CO_2 removal (%)	PCO_2 (atm)
A	**30**	**50**	**7.02**	**11.2**	**18.2**	**2.03**
B	**30**	**50**	**6.90**	**10.3**	**18.2**	**1.87**
C	**30**	**50**	**6.87**	**10.8**	**18.2**	**1.96**
	Output					
	CO_2 Lost (%)	Vol. Liq. End (mL)	Weight Spl. End (g)	Pressure End (atm)	CO_2 removal End (%)	PCO_2 (atm)
A	**83**	**45**	**6.81**	**9.05**	**3.9**	**0.35**

B	82	45	6.84	8.64	4.0	0.35
C	82	43	6.80	8.57	4.1	0.35

A removal of 82 % of CO_2 was achieved after a reaction time of 30 min.

EXAMPLE 2 – Wet carbonation of serpentinite

This experiment describes the feasibility of the process for the treatment of a batch of gas containing 18.2% of carbon dioxide during 15 minutes. The gas liquid ratio (GLR) was fixed at 300% which represents a volume of carbon dioxide containing gas of 225 mL and a volume of 75 mL of water. The resulting aqueous slurry had a 15 wt% concentration of solid material. Reaction temperature was set at ambient temperature (18-25℃). A pressure of 10.5 bars was applied which represented an amount of 0.78 g of CO_2 at 20℃. Once the pressure reached, all valves of the reactor were closed and reaction occurred for 15 minutes. The resulting carbon dioxide depleted gas was then sampled through a bag. The carbon dioxide concentration in the carbon dioxide depleted gas was measured by a CO_2 analyzer. The resulting aqueous slurry was filtered and samples were taken for analysis.

Reaction under ambient temperature at 10.5 bars during 15 minutes showed an efficiency of 88 ± 1% on the CO_2 removal as seen in Table 3.

Table 3: Carbon dioxide mass balance for 15 minutes reaction at 10.5 bars (*number of assays* = 3)

	Entry	Exit	CO_2 treated	Efficiency
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

EXAMPLE 3 – Optimisation of thermal pre-treatment of serpentinite before wet carbonation

Another series of experiments was performed to show that the thermal pre-treatment of the alkaline earth metal containing material favors a good removal of carbon dioxide from the carbon dioxide containing gas.

A serpentinite based mining residue was used as alkaline earth metal containing material. Firstly, depending on the grain size, the residue was crushed, and then grinded. The best results were obtained with samples with a particle size lower than 45µm (median size 10µm). In order to obtain a chemically reactive material, the serpentinite based mining residue has to be further pre-treated to allow dehydroxylation of the serpentinite. By removing water from the various crystalline structures of the minerals, the chemical structure of the sample is altered and thus lowers the bound energies. The heat activation of hydrated silicates is well known to favour chemical activation prior to lixiviation [Nagamori et al. (1980) *Activation of magnesia in serpentine by calcination and the chemical utilization of asbestos tailings* – A review. CIM Bulletin 73, pp.144-156].

The optimization of thermal pre-treatment was carried out following the magnesium concentration after leaching dissolved in water (beaker). Referring to Figs 5 and 6, influence of temperature and pre-treatment time, and the pulp density during the extraction for 30 minutes in water with stirring at 600 rpm have been studied. According to a thermogravimetric analysis, the major weight loss of the sample studied is observed at 650℃. Essays on heat activation showed that best results were obtained after a 30 minutes treatment at 650℃ with a mass loss around 10%.

EXAMPLE 4 – Optimisation of reaction parameters for wet carbonation

Another series of experiments has been performed to optimize reaction parameters including carbonation pressure, reaction time, gas/liquid ratio (GLR) and pulp density of the aqueous slurry. To enhance gaseous carbon dioxide solubility in water, the reaction temperature was set at room temperature (18-25℃) as solubility is increased at lower temperatures. Pressure is a key process parameter as it influences the quantity of carbon dioxide introduced in the reactor.

The experiments were conducted with a carbon dioxide containing gas whose characteristics are comparable to a cement plant flue gas. The composition is respectively 18.2% CO_2, 4.11% O_2, and 77.69% N_2. Reactions were realized in a 300 mL stirred reactor from Parr Instrument Company, Moline IL USA.

Pressure

Tests on pressure effect showed that working at low pressure was not affecting the reaction efficiency. Indeed, lowering pressure results in introducing a small quantity of carbon dioxide in the reactor. For batch wise experiments, in order to maintain a certain quantity of carbon dioxide introduced in the reactor, pressure was set to 10.5 bars.

GLR and pulp density

Parameters such as the gas/liquid ratio (GLR) and the pulp density had been determined by a set of experiments with a reaction time of 30 minutes. Decreasing the GLR did not impact the carbon dioxide removal from the flue gas but decreased the quantity of carbon dioxide introduced in the reactor. On the other hand, the quantity of flue gas treated was lower when pulp density was set at 5%. In order to increase the quantity of gas treated, experiments on GLR and pulp density were realized with successive batch of gas.

As the objective is to form alkaline earth metal carbonates with a resale potential, it is important to have the purest final product possible. Experiments with a GLR of 100% and a pulp density of 15% showed that a significant amount of carbonates was precipitated within the reactor. However, it may be desired to precipitate carbonates outside of the reactor so as to easily separate precipitable carbonates and obtain thereafter carbonates with high purity of about 95%. Fig 7 shows that good yields of CO_2 removal and a high concentration of magnesium in solution are encountered with an aqueous slurry of 15% pulp density and a GLR of 300%.

Once the principal parameters of the reaction were settled, the reaction time was reduced.

Reaction time

A series of experiments was carried out to reduce the reaction time. Fig 8 shows the carbon dioxide removal results. The removal was 56% for a reaction time of 5 min, and 83% for a reaction time of 10 min. Same efficiencies as observed for 30 minutes were respectively 18.2% CO_2, 4.11% O_2, and 77.69% N_2. Reactions were realized in a 300 mL stirred reactor from Parr Instrument Company, Moline IL USA.

Pressure

Tests on pressure effect showed that working at low pressure was not affecting the reaction efficiency. Indeed, lowering pressure results in introducing a small quantity of carbon dioxide in the reactor. For batch wise experiments, in order to maintain a certain quantity of carbon dioxide introduced in the reactor, pressure was set to 10.5 bars.

GLR and pulp density

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Reaction time

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Precipitation conditions have been set at 40℃ unde r 300 rpm agitation. The filtered solid phase, after contacting 6 batches of carbon dioxide containing gas, is grinded and heated in order to improve further magnesium lixiviation. Then, the treated solid phase is recirculated in the reactor for contacting 6 more batches of carbon dioxide containing gas.

A total of 12 batches of carbon dioxide containing gas was therefore treated by the same solid phase. The aqueous phase was filtered after contacting two batches of carbon dioxide containing gas and fresh water was used after contacting two batches of carbon dioxide containing gas.

Results are summarized in Table 4. Carbonation of the solid material is 64% after contact with 12 batches assuming that all the magnesium contained in the aqueous phase precipitated.

Table 4: Amount of CO_2 treated (gCO_2), efficiency of the CO_2 removal and Mg lixiviation over 12 batches of 15min.

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	Batch 7	Batch 8	Batch 9	Batch 10	Batch 11	Batch 12	Cumulative
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Efficiency	86%	87%	87%	77%	72%	51%	75%	65%	53%	34%	37%	21%	62%
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

EXAMPLE 7 - Dry gas-solid carbonation

Example 7 describes dry gas-solid carbonation experiments according to optional embodiments of the present invention.

In this series of experiments, the alkaline earth metal containing material was a chrysotile mining residue coming from the region of Thetford Mines directly from the exit of the residue conveyor. The chrysotile residue was crushed and grinded to a mini-particle size of about 50 microns. The reaction took place in a *minibench top reactor 4560* of *Parr Instrument Company*. After the reaction, the gas was sampled in a *Tedlar Bags* of 3.8 L equipped with an *on / off valve*. The carbon dioxide concentration in the outlet gas was measured with a CO_2, *Quantek Instruments, model 906*.

The optimization of different parameters that can have significant influence on direct dry gas-solid carbonation was performed in both conventional single variable at a time method and with the statistical response surface methodology.

Optimization of parameters using a conventional single variable method

A series of experiments was carried out to optimize the most suitable conditions for direct dry gas-solid carbonation with conventional single variable variation at a time. The carbonation performance at different temperatures and pressures was optimized on the basis of percentage of CO_2 removal (dependent variable). Optimized conditions were evaluated for raw, non magnetic (Non-Mag) and heat treated samples. The optimized conditions for each type of sample were given in Table 5.

Table 5 Optimized conditions for direct dry gas-solid carbonation with different type of samples

Sample type	Sample size (g)	Heat-treatment (℃, min)	Temperature (℃)	Pressure (atm)	Time (h)	Average CO_2 removal (%)
Raw	**25**	**No**	**200**	**5**	**6**	**27.7 ± 0.6**
Non-Mag	**25**	**No**	**200**	**5**	**6**	**28.9 ± 0.6**

Raw	**25**	**630, 30**	**200**	**5**	**6**	**36.8 ± 2.4**

The operating conditions for direct dry carbonation were optimized at 5 atm pressure and 200°C temperature for 6 h duration. A maximum CO_2 removal of 36.8% was obtained with raw heat treated (at 630°C for 30 min and grinded) sample.

Optimization of parameters using a Box-Behnken design

The independent variable selected are temperature (X1), pressure (X2) and time (X3) and the independent response variable selected are CO_2 removal, Y1(%) and pressure variation, Y2 (kPa). Since the removal CO_2 is the key factor in this experiment, the present study focused on the percentage removal of CO_2. So, the percentage of CO_2 removal was chosen as the major response surface in this model. Heat treated (630°C for 30 min) sample of 25 g was used for all runs.

Fig 10 shows the response surface graph for CO_2 removal (%) and from the figure it is clear that the CO_2 removal (%) is at its maximum at low pressure and higher temperature region. The optimal conditions and validation of optimized value are presented in Table 6. The variance analysis of the quadratic regression parameter for the predicted response surface of CO_2 removal (%) was analyzed by ANOVA.

The Model F-value of 30.56 and low probability value "Prob > F" less than 0.050 implies the model is significant. The value of multiple regression coefficients ($R^2 = 0.9752$) shows that only 2.5% of the total variation could not be explained by the empirical model. This model could explain 97.5% of the variability of response. The R^2 (0.9752) for CO_2 removal (%) was found in reasonable agreement with the adjusted R^2 value (0.9433).The predicted R^2 (0.70) was in reasonable agreement with adjusted R^2.

The optimized conditions for direct dry gas-solid carbonation by using Box-Behnken design was obtained at 258°C, 5.6 atm for 310 min. A CO_2 removal of 40.1% was predicted at the above conditions.

The validation of the model shows a CO_2 removal of 37%, which is close to the predicted value.

Table 6 **Validation experiments of the response surface model (RSM)**

Experiments (No.)	Temperature (℃)	Pressure (atm)	Time (min)	CO_2 removal (%)
RSM Model	**258 ***	**5.53***	**310***	**40.1****
A	**258**	**5.53**	**310**	**37.9**
B	**258**	**5.53**	**310**	**36.2**
C	**258**	**5.53**	**310**	**37.4**
Average				**37.1 ± 0.8**

** Optimum values of variables selected by the model.*

*** Predicted values for each response according to the model.*

Carbonation studies were also conducted with raw and non magnetic sample at optimized conditions obtained from response surface methodology. The experiments and results are given in Table 7 and it shows that in optimized conditions, the CO_2 removal (%) for three type of samples are in close range. This indicates that the pre-treatment of sample does not make any significant effect in CO_2 removal (%).

Table 7 **Experimental conditions and results for direct dry gas-solid carbonation of different type of samples at optimized conditions established by response surface methodology**

Sample type	Temperature (℃)	Pressure (atm)	Time (min)	CO_2 removal (%)
Raw	**258**	**3.95**	**310**	**35.7 ± 1.1**
Non-Mag	**258**	**2.96**	**310**	**35.7**
Heat treated	**258**	**1.97**	**310**	**37.1 ± 0.8**

Since time duration for carbonation in optimized conditions seems to be very long 310 min, carbonation assays were carried out for shorter reaction time to verify the time dependency of the rate of dry carbonation. The experiments and results are presented in Table 8.

Table 8 Experimental conditions and results for direct dry carbonation of raw sample at optimized temperature and pressure for 15 min duration

Run	Temperature (℃)	Pressure (atm)	Time (min)	CO_2 removal (%)
A	**258**	**3.95**	**15**	**36.3**
B	**258**	**2.96**	**15**	**39.0**
C	**258**	**1.97**	**15**	**33.5**
Average				**36.3 ± 2.7**

From the results, it was found that the major percentage of reaction occurs during the initial stage of carbonation reaction. The reaction achieved about 36% of CO_2 removal at 258°C, 5.53 atm within 15 min. This would suggest that major percentage of carbonation takes place within a time limit after which the reaction might become less important. The pressure variation curve given in Fig 11 supports the above statement. The sudden decrease in pressure at the initial minutes indicates that the reaction occur fast at initial and then the decrease in pressure becoming very slow or constant indicates the carbonation occur very slow or attained equilibrium. The increase in pressure and temperature right after the addition of the CO_2 gas mixture might be due to the exothermic character of the reaction. The decrease in rate of reaction after certain time might be due to the formation of product layer, which might further hinder the inward diffusion of CO_2 and outward diffusion of water. The lesser surface renewal rate could also diminish the rate of carbonation, which could be increased by increasing the rate of particle attrition and abrasion through well mixing.

EXAMPLE 8 – Comparison of CO_2 removal efficiencies

Experiments have been performed to compare the CO_2 removal efficiency for wet and dry carbonation of various alkaline earth metal containing materials.

Results for wet carbonation are shown in Table 9 and results for dry carbonation are shown in Table 10.

Table 9 Wet carbonation of 150 g/L of solid during 15 minutes at ambient temperature, P= 10.5 bars

Sample/Test	Thermal pre-treatment	Average CO_2 input (g)	Average CO_2 output(g)	Average %CO2 uptake	Std
Bignel Stone-pit (St urbain) - Anorthosite	no	0.78	0.52	34.51	2.47
Bouchard stone-pit (St Urbain)-Anorthosite	no	0.78	0.43	44.37	10.18
Old Gen.electrique stone-pit (St Urbain)-Anorthosite	no	0.76	0.45	40.51	15.49
andesine (BML Charlesbourg stone-pit)	no	0.78	0.47	39.77	7.66
concrete brick	no	0.76	0.34	55.64	11.85
concrete with aggregates	no	0.79	0.29	63.41	2.59
concrete	no	0.78	0.17	78.44	1.21
steelmaking slag	no	0.76	0.12	84.51	4.23
Red brick	no	0.78	0.43	44.71	9.60
Antigorite (Thetford Mines stone-pit)	yes	0.78	0.32	58.89	2.94
sandstone (Montmagny stone-pit)	no	0.79	0.40	49.35	2.47
worn MgO brick (steelmaking)	no	0.77	0.43	44.62	2.23
Wollastonite (Black Lake stone-pit)	no	0.78	0.46	40.80	2.04
olivine sand	no	0.77	0.47	38.78	1.94
Granite (Aguanish stone-pit)	no	0.77	0.49	37.06	1.85
Magnesium rich Basalt (St Joseph de Beauce stone-pit)	no	0.80	0.54	32.90	1.64
Calcium rich Basalt RayCar (St Flavie stone-pit)	no	0.77	0.55	28.68	1.43

Granite (Aguanish stone-pit)	**yes**	0.77	0.57	**25.12**	**1.26**
CaO Rotary kiln dust	**no**	0.77	0.04	**95.38**	**4.77**
MgO Rotary kiln dust	**no**	0.75	0.05	**93.20**	**4.66**

Table 10: Dry carbonation of 1.5 g of solid during 30 minutes at T=258°C, P= 4 bars

Sample Test	Thermal *pretreatment*	Average CO_2 *Input (g)*	Average CO_2 *output (g)*	Average CO_2 *utpake (%)*	Std
Bignel Stone-pit (St urbain) - Anorthosite	**no**	0.17	0.09	**43.37**	**6.74**
concrete	**no**	0.16	0.02	**74.83**	**1.58**
concrete brick	**no**	0.17	0.04	**74.79**	**6.63**
concrete with aggregates	**no**	0.16	0.07	**58.03**	**4.66**
Bouchard stone-pit (St Urbain)-Anorthosite	**no**	0.17	0.09	**46.98**	**5.44**
Old Gen. Electrique (St Urbain)	**no**	0.18	0.03	**81.14**	**2.95**
Andesine (BML Charlesbourg stone-pit	**no**	0.17	0.10	**39.90**	**10.30**
Red brick	**no**	0.18	0.10	**41.07**	**12.56**
steelmaking slag	**no**	0.18	0.09	**47.18**	**16.72**
worn MgO brick (steelmaking)	**no**	0.18	0.05	**70.67**	**0.40**
CaO Rotary kiln dust	**no**	0.16	0.10	**37.99**	
sandstone (Montmagny stone-pit)	**no**	0.22	0.14	**34.08**	**0.78**
Calcium rich Basalt RayCar (St Flavie stone-pit)	**no**	0.22	0.13	**38.75**	**1.92**
***Magnesium rich Basalt* (St Joseph de Beauce stone-pit)**	**no**	0.22	0.13	**40.38**	**0.39**
Granite (Aguanish stone-pit)	***no***	0.22	*0.13*	**40.10**	**0.78**
Granite (Aguanish stone-pit)	**yes**	0.22	0.13	**41.48**	**1.95**
olivine sand	**no**	0.22	0.12	**43.13**	**1.17**
Wollastonite (Black Lake stone-pit)	**no**	0.22	0.12	**43.13**	**1.17**
Antigorite (Thetford Mines stone-pit)	**yes**	0.22	0.13	**42.31**	**0.78**
Serpentinite (Black Lake)	**no**	0.22	0.13	**42.05**	**5.07**
Serpentinite (Black Lake)	**yes**	0.22	0.14	**23.2**	**5.82**
MgO Rotary kiln dust	**no**	0.22	0.14	**37.34**	

CLAIMS

1. A process for sequestering carbon dioxide from a carbon dioxide containing gas, the process comprising:

   contacting the carbon dioxide containing gas with an aqueous slurry comprising an alkaline earth metal containing material in a carbonation unit for carbonation of at least a portion of an alkaline earth metal to produce a carbon dioxide depleted gas and a carbonate loaded slurry comprising precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;

   removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into an aqueous phase comprising the precipitable carbonates and a solid phase; and

   supplying the aqueous phase to a precipitation unit and precipitating alkaline earth metal carbonates in the precipitation unit to produce a precipitation slurry.

2. The process of claim 1, wherein the aqueous phase comprises the precipitable carbonates and is substantially exempt of precipitated alkaline earth metal carbonates.

3. The process of claim 1 or 2, further comprising the step of agitating the aqueous slurry comprising an alkaline earth metal containing material during the step of contacting in the carbonation unit.

4. The process of any one of claims 1 to 3, further comprising the step of agitating the aqueous phase during the step of precipitating the alkaline earth metal carbonates in the precipitation unit.

5. The process of any one of claims 1 to 4, further comprising the step of mixing the alkaline earth metal containing material with water, prior to the step of contacting, to dissolve alkaline earth metal ions in aqueous phase and form the aqueous slurry.

6. The process of any one of claims 1 to 4, further comprising the step of mixing the alkaline earth metal containing material with water, simultaneously to the step of

contacting, to dissolve alkaline earth metal ions in aqueous phase and form the aqueous slurry within the carbonation unit.

7. The process of claim 5 or 6, wherein the step of mixing is performed so as to form the aqueous slurry having a mass concentration between 25 g/L and 300 g/L in grams of total solids per liter of aqueous slurry.

8. The process of any one of claims 1 to 7, further comprising:

   separating the precipitation slurry into a solid stream comprising the alkaline earth metal carbonates and an aqueous stream.

9. The process of claim 8, further comprising drying the solid stream comprising the alkaline earth metal carbonates.

10. The process of claim 8 or 9, further comprising:

    recycling at least a portion of the aqueous stream into the carbonation unit.

11. The process of any one of claims 1 to 10, further comprising:

    recycling at least a portion of the solid phase into the carbonation unit as at least part of the alkaline earth metal containing material for contacting with the carbon dioxide containing gas.

12. The process of any one of claims 1 to 11, further comprising:

    thermally pre-treating the alkaline earth metal containing material for dehydroxylation thereof, to produce a pre-treated alkaline metal earth containing material for contacting with the carbon dioxide containing gas.

13. The process of claim 12, wherein the step of thermally pre-treating the alkaline earth metal containing material comprises heating the alkaline metal earth containing material at a temperature between about 500℃ and a bout 800℃ during a pre-treating time of about 10 minutes to about 60 minutes.

14. The process of claim 13, wherein the temperature is between about 600℃ and about 700℃ and the pre-treating time is between about 15 minutes and about 40 minutes.

15. The process of any one of claims 12 to 14, further comprising:

    crushing and/or grinding the alkaline metal earth containing material prior to the step of contacting with the carbon dioxide containing gas.

16. The process of claim 15, wherein the step of crushing and/or grinding is performed prior to the step of thermally pre-treating the alkaline earth metal containing material.

17. The process of claim 15 or 16, wherein the step of crushing and/or grinding is performed to obtain solid particles having a median particle size between about 10 µm and about 45 µm and so as to obtain 90 % of the solid particles having a particle size between about 0 µm and about 75 µm.

18. The process of any one of claims 1 to 17, wherein the carbon dioxide containing gas is derived from industrial emissions and has a carbon dioxide concentration between 1% and 30%.

19. The process of any one of claims 1 to 18, further comprising:

    controlling at least one of a carbonation temperature, an agitation speed and a carbonation pressure in the carbonation unit.

20. The process of claim 19, wherein the step of contacting in the carbonation unit is performed at the carbonation temperature between about 10℃ and about 40℃.

21. The process of claim 19 or 20, wherein the carbonation temperature is between about 20℃ and about 30℃.

22. The process of any one of claims 19 to 21, wherein the step of contacting in the carbonation unit is performed at the carbonation pressure between about 1 bar and about 20 bars.

23. The process of claim 22, wherein the carbonation pressure is between about 2 bars and about 12 bars.

24. The process of any one of claims 19 to 23, wherein the agitation speed in the carbonation unit is between about 400 rpm and about 800 rpm.

25. The process of claim 24, wherein the agitation speed is between about 500 rpm and about 650 rpm.

26. The process of any one of claims 1 to 25, wherein the step of precipitating is performed at a precipitation temperature between about 20℃ and about 80℃ for a precipitation time between about 0.5 hours and about 12 hours.

27. The process of claim 26, wherein the step of precipitating comprises agitating the aqueous phase.

28. The process of any one of claims 1 to 27, wherein the alkaline earth metal comprises calcium or magnesium.

29. The process of any one of claims 1 to 28, wherein the alkaline earth metal containing material comprises at least one of sandstone, granite, anorthosite, basalt, serpentinite, peridotite, serpentinized peridotite, ophiolitic rocks, mafic and ultramafic rocks, rocks containing more than 10% of pyroxene and peridot, calcium silicate, magnesium silicate, feldspar, plagioclase feldspar, peridot, pyroxene, olivine, serpentine, wollastonite, calcium oxide, magnesium oxide, brucite, mafic and ultramafic minerals, steelmaking slag, steelmaking worn MgO brick, rotary kiln dust (CKD, LKD), waste cement, waste concrete, construction and demolition waste, concrete with aggregates, concrete brick, concrete, red brick, phyllosilicate mining residue and chrysotile mining residue.

30. The process of any one of claims 1 to 29, comprising supplying continuously the carbon dioxide containing gas to the carbonation unit.

31. The process of claim 30, comprising controlling or managing a maximal quantity of dissolved carbon dioxide in the carbonate loaded slurry produced in the carbonation unit, the maximal quantity of dissolved carbon dioxide being chosen to reduce or avoid precipitation of the alkaline earth metal carbonates in the carbonation unit.

32. The process of claim 31, wherein the maximal quantity of dissolved carbon dioxide is at most 5 g/L.

33. The process of any one of claims 1 to 29, wherein the carbon dioxide containing gas comprises a plurality of carbon dioxide containing gas portions, the process comprising:

    supplying at least one carbon dioxide containing gas portion to the carbonation unit;

    contacting the aqueous slurry with the at least one carbon dioxide containing gas portion in the carbonation unit for production of the carbonate loaded slurry;

    removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into the aqueous phase comprising the precipitable carbonates and the solid phase; and

    recycling the solid phase to the carbonation unit and supplying water to the carbonation unit to form a new portion of aqueous slurry;

    contacting the new portion of aqueous slurry with another carbon dioxide containing gas portion for production of the carbonate loaded slurry.

34. The process of any one of claims 1 to 29, wherein the carbon dioxide containing gas is supplied to the carbonation unit as a plurality of carbon dioxide containing gas portions, the process comprising:

    contacting the aqueous slurry with at least one carbon dioxide containing gas portion in the carbonation unit for production of the carbonate loaded slurry;

    removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into the aqueous phase comprising the precipitable carbonates and the solid phase; and

    supplying the aqueous phase comprising the precipitable carbonates to the precipitation unit, precipitating the alkaline earth metal carbonates in the precipitation unit to produce the precipitation slurry and separating the precipitation slurry into a solid stream comprising the alkaline earth metal carbonates and an aqueous stream;

recycling the solid phase and the aqueous stream to the carbonation unit to produce a new portion of aqueous slurry and contacting the new portion of aqueous slurry with another carbon dioxide containing gas portion for production of the carbonate loaded slurry.

35. The process of claim 34, further comprising supplying water to the carbonation unit as a make up stream of the new portion of aqueous slurry.

36. The process of any one of claims 33 to 35, wherein the step of contacting in the carbonation unit is performed for a maximal gas contact time, the maximal gas contact time being controlled or managed to reduce or avoid precipitation of the alkaline earth metal carbonates in the carbonation unit.

37. The process of claim 36, wherein the maximal gas contact time is between about 1 minute and about 60 minutes.

38. The process of any one of claims 33 to 37, further comprising crushing and/or grinding the solid phase prior to the step of recycling to the carbonation unit to produce the new portion of aqueous slurry.

39. A process for sequestering carbon dioxide from a carbon dioxide containing gas, the process comprising:

contacting the carbon dioxide containing gas with an aqueous slurry comprising a magnesium containing material in a carbonation unit at a carbonation temperature between about 10ºC and about 40ºC and a carbonation pressure between about 1 bar and about 20 bars, for carbonation of at least a portion of magnesium to produce a carbon dioxide depleted gas and a carbonate loaded slurry comprising precipitable carbonates and substantially exempt of precipitated magnesium carbonates.

40. The process of claim 39, further comprising:

removing the carbonate loaded slurry from the carbonation unit and separating the carbonate loaded slurry into a solid phase and an aqueous phase comprising precipitable carbonates and substantially exempt of precipitated magnesium carbonates; and

supplying the aqueous phase to a precipitation unit and precipitating magnesium carbonates in the precipitation unit to produce a precipitation slurry comprising the precipitated magnesium carbonates.

41. The process of claim 40, further comprising separating the precipitation slurry into a solid stream comprising the precipitated magnesium carbonates and an aqueous stream.

42. The process of any one of claims 39 to 41, further comprising one or more features as defined in any one of claims 1 to 38.

43. A process for sequestering carbon dioxide from a carbon dioxide containing gas, the process comprising:

contacting the carbon dioxide containing gas with an alkaline earth metal containing material in a substantially dry form in at least one carbonation unit at a carbonation temperature between about 200℃ and about 500℃ and a carbonation pressure between about 1 bar and about 20 bars, for carbonation thereof to produce carbonates and a carbon dioxide depleted gas.

44. A method for sequestering carbon dioxide from industrial emissions by contacting the industrial emissions with magnesium silicate material, in wet or dry form, to produce a carbon dioxide depleted gas and a carbonated magnesium silicate material.

45. A method for manufacturing alkaline earth metal carbonates, the method comprising:

a contacting stage wherein industrial emissions comprising carbon dioxide are contacted with an aqueous slurry comprising an alkaline earth metal containing material, to produce a carbon dioxide depleted gas and an alkaline earth metal carbonate stream substantially exempt of precipitated alkaline earth metal carbonates;

a precipitation stage wherein alkaline earth metal carbonates are precipitated from the alkaline earth metal carbonate stream, thereby producing a precipitation slurry; and

a separation stage wherein the precipitation slurry is separated into the precipitated alkaline earth metal carbonates and an aqueous stream.

46. A method for manufacturing alkaline earth metal carbonates, the method comprising:

a contacting stage wherein industrial emissions comprising carbon dioxide are contacted with an aqueous slurry comprising an alkaline earth metal containing material, to produce a carbon dioxide depleted gas and an alkaline earth metal carbonate stream comprising precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;

a first separation stage wherein the alkaline earth metal carbonate stream is separated into a solid phase and an aqueous phase comprising the precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates;

a recycling stage wherein the solid phase is recycled to the carbonation stage as at least a portion of the alkaline earth metal containing material;

a precipitation stage wherein alkaline earth metal carbonates are precipitated from the aqueous phase, thereby producing a precipitation slurry comprising the precipitated alkaline earth metal carbonates; and

a second separation stage wherein the precipitation slurry is separated into the precipitated alkaline earth metal carbonates and an aqueous stream .

47. A carbon dioxide sequestration system for sequestering carbon dioxide from a carbon dioxide containing gas, the system comprising:

at least one carbonation unit having:

a gas inlet for receiving the carbon dioxide containing gas,

a slurry inlet for receiving an aqueous slurry comprising an alkaline earth metal containing material,

a carbonation vessel for the carbonation of at least a portion of an alkaline earth metal of the aqueous slurry with carbon dioxide to produce a carbon dioxide depleted gas and a carbonate loaded slurry comprising precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates,

a slurry outlet for releasing the carbonate loaded slurry comprising precipitable carbonates, and

a gas outlet for releasing the carbon dioxide depleted gas;

a separation unit having:

a slurry inlet for receiving the carbonate loaded slurry comprising precipitable carbonates from the slurry outlet of the at least one carbonation unit,

a separation chamber for separation of the carbonate loaded slurry comprising precipitable carbonates into a solid phase and an aqueous phase comprising the precipitable carbonates and substantially exempt of precipitated alkaline earth metal carbonates,

a liquid outlet for releasing the aqueous phase, and

a solid outlet for releasing the solid phase; and

a precipitation unit having:

a slurry inlet for receiving the aqueous phase comprising the precipitable carbonates from the liquid outlet of the separation unit,

a precipitation chamber for precipitation of the alkaline earth metal carbonates and formation of a precipitation slurry, and a liquid outlet for releasing the precipitation slurry.

48. Use of a magnesium containing material in the form of an aqueous slurry to contact and sequestrate carbon dioxide from a carbon dioxide containing gas at a temperature between about 20℃ and about 30℃ and a pressure between about 2 bars and about 12 bars to form magnesium carbonates.

49. Use of a phyllosilicate mining residue to sequestrate carbon dioxide from industrial emissions and produce magnesium carbonates.

50. The use of claim 49, wherein the phyllosilicate mining residue comprises at least one of lizardite, antigorite, brucite, iron oxide, chromium oxide and chrysotile.

51. A precipitated calcium or magnesium carbonate (PCC or PMC) produced by contacting a calcium or magnesium containing material in wet form with carbon dioxide from industrial emissions in a carbonation unit to form a carbonate loaded slurry, and precipitating the calcium or magnesium carbonate from the carbonate loaded slurry in a precipitation unit.

52. A precipitated calcium or magnesium carbonate (PCC or PMC) comprising at least 95 wt% of calcium or magnesium carbonate in dry form or hydrated form.

53. The PCC or PMC of claim 52, produced by the process as defined in any one of claims 1 to 46.

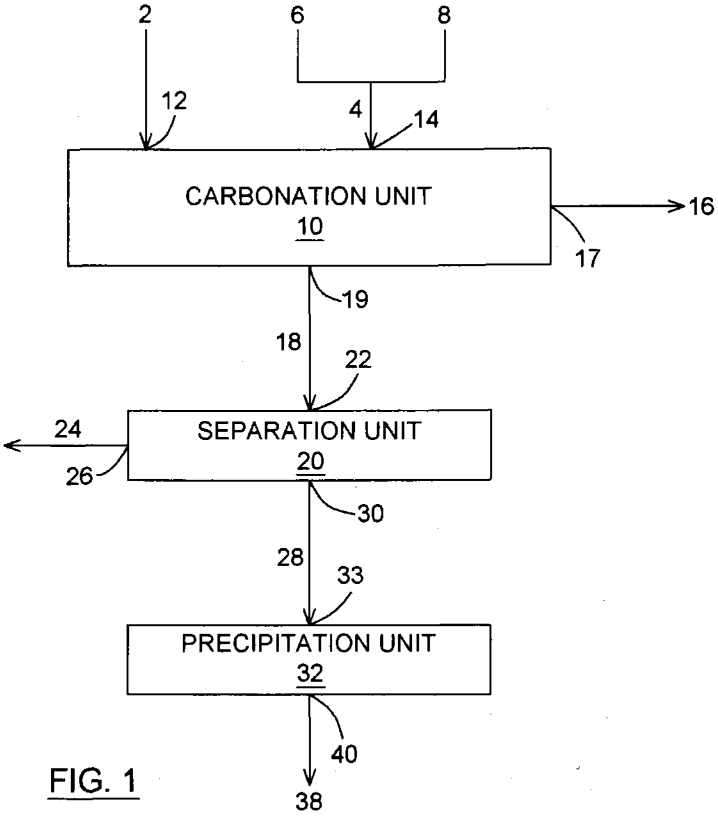

2
6
8
12
4
14
CARBONATION UNIT
10
16
17
19
18
22
24
SEPARATION UNIT
20
26
30
28
33
PRECIPITATION UNIT
32
40
38

FIG. 1

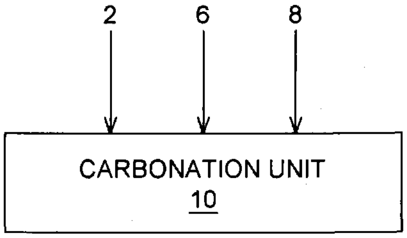

2
6
8
CARBONATION UNIT
10

FIG. 2

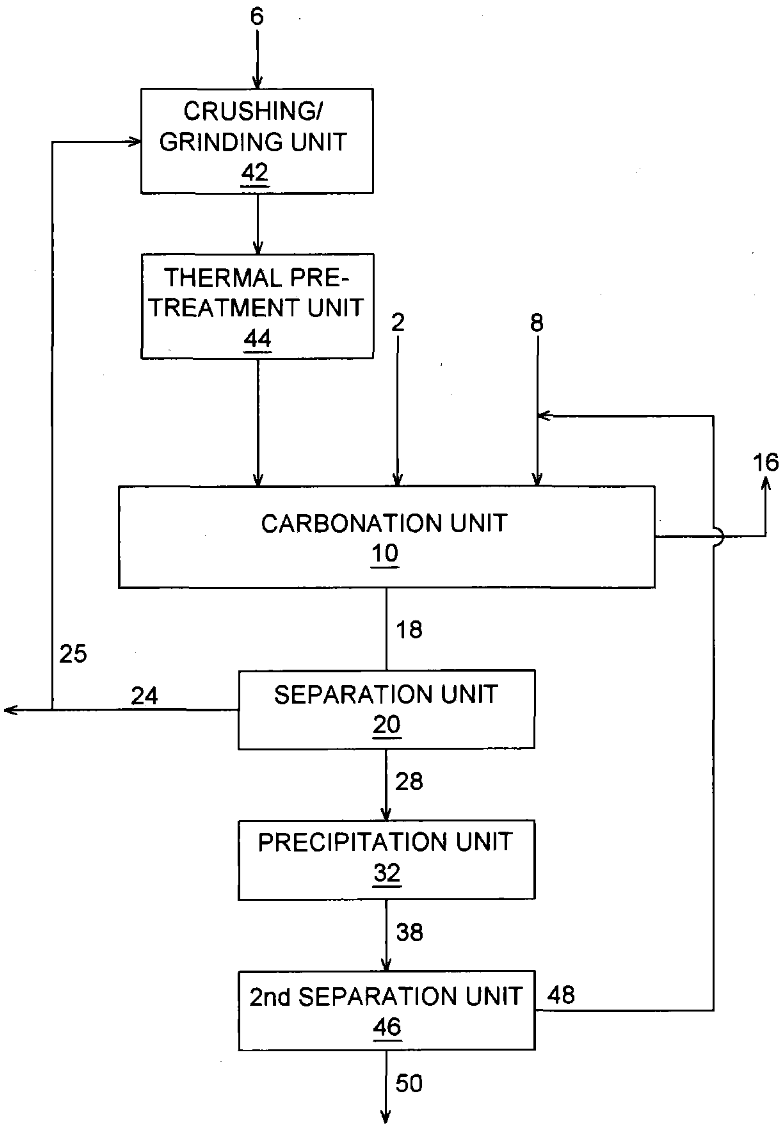

6
CRUSHING/ GRINDING UNIT 42
THERMAL PRE-TREATMENT UNIT 44
2
8
16
CARBONATION UNIT 10
18
25
24
SEPARATION UNIT 20
28
PRECIPITATION UNIT 32
38
2nd SEPARATION UNIT 46
48
50

FIG. 3

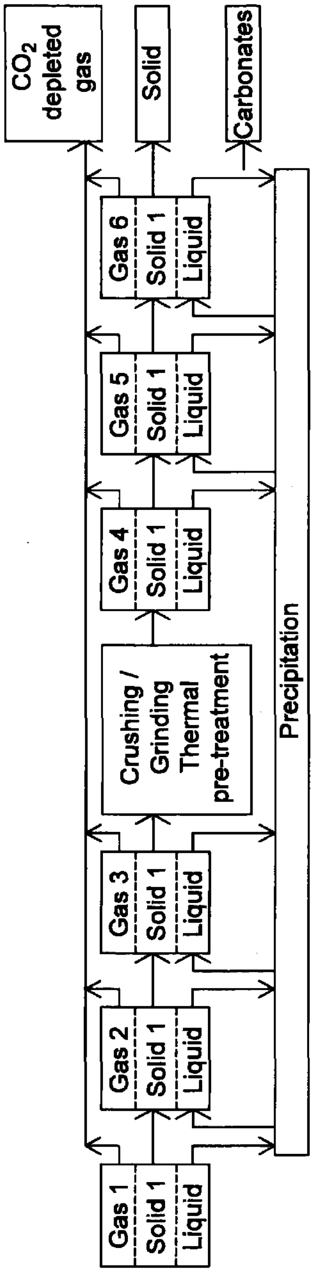

Gas 1
Solid 1
Liquid
Gas 2
Solid 1
Liquid
Gas 3
Solid 1
Liquid
Crushing / Grinding Thermal pre-treatment
Gas 4
Solid 1
Liquid
Gas 5
Solid 1
Liquid
Gas 6
Solid 1
Liquid
Precipitation
CO_2 depleted gas
Solid
Carbonates

FIG. 4

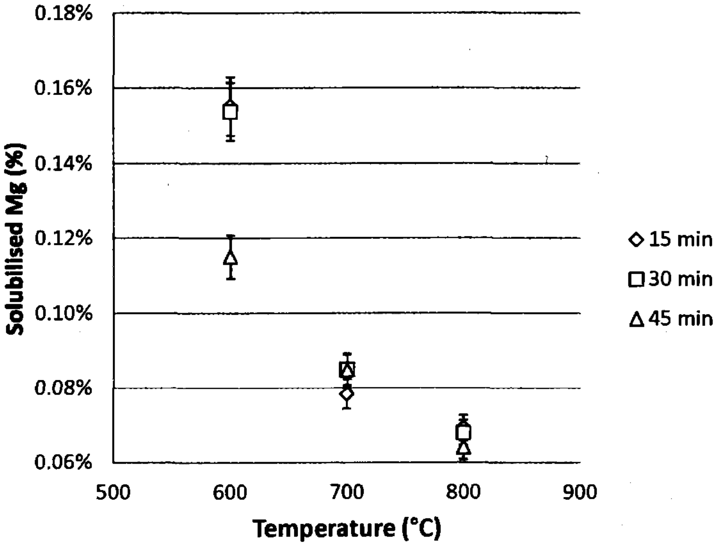

0.18%
0.16%
0.14%
0.12%
0.10%
0.08%
0.06%
Solubilised Mg (%)
500
600
700
800
900
Temperature (°C)
◇ 15 min
□ 30 min
△ 45 min

FIG. 5

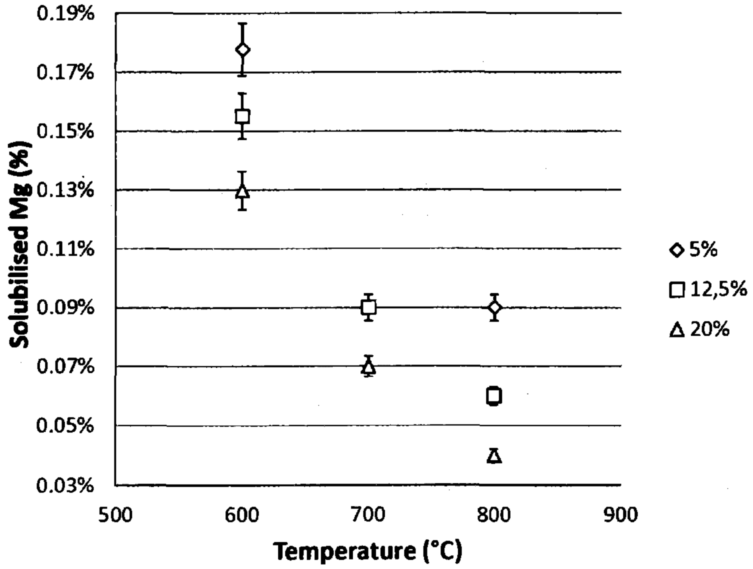

0.19%
0.17%
0.15%
0.13%
0.11%
0.09%
0.07%
0.05%
0.03%
Solubilised Mg (%)
500
600
700
800
900
Temperature (°C)
◇ 5%
□ 12,5%
△ 20%

FIG. 6

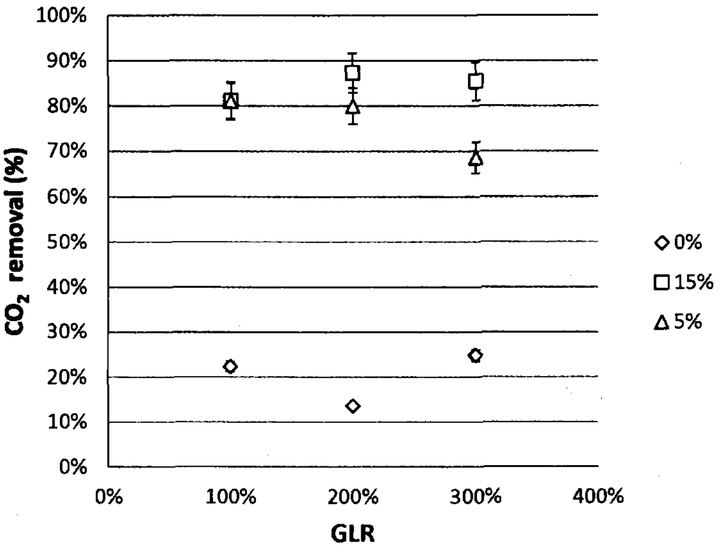

100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
CO$_2$ removal (%)
0%
100%
200%
300%
400%
GLR
◇ 0%
□ 15%
△ 5%

FIG. 7

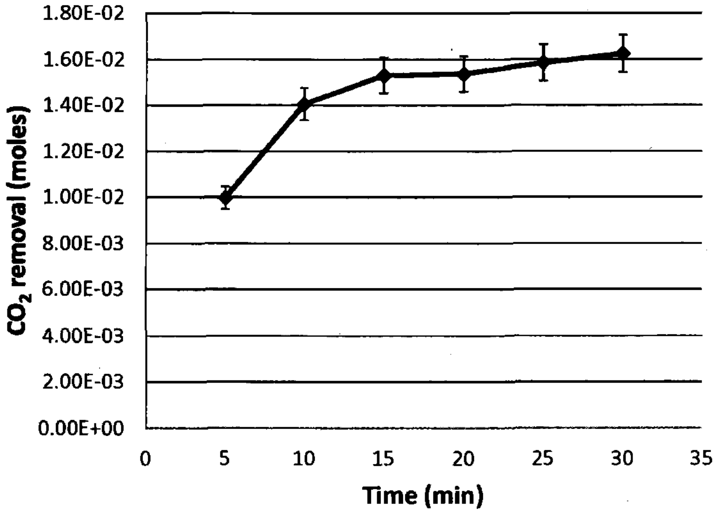

1.80E-02
1.60E-02
1.40E-02
1.20E-02
1.00E-02
8.00E-03
6.00E-03
4.00E-03
2.00E-03
0.00E+00
CO$_2$ removal (moles)
0
5
10
15
20
25
30
35
Time (min)

FIG. 8

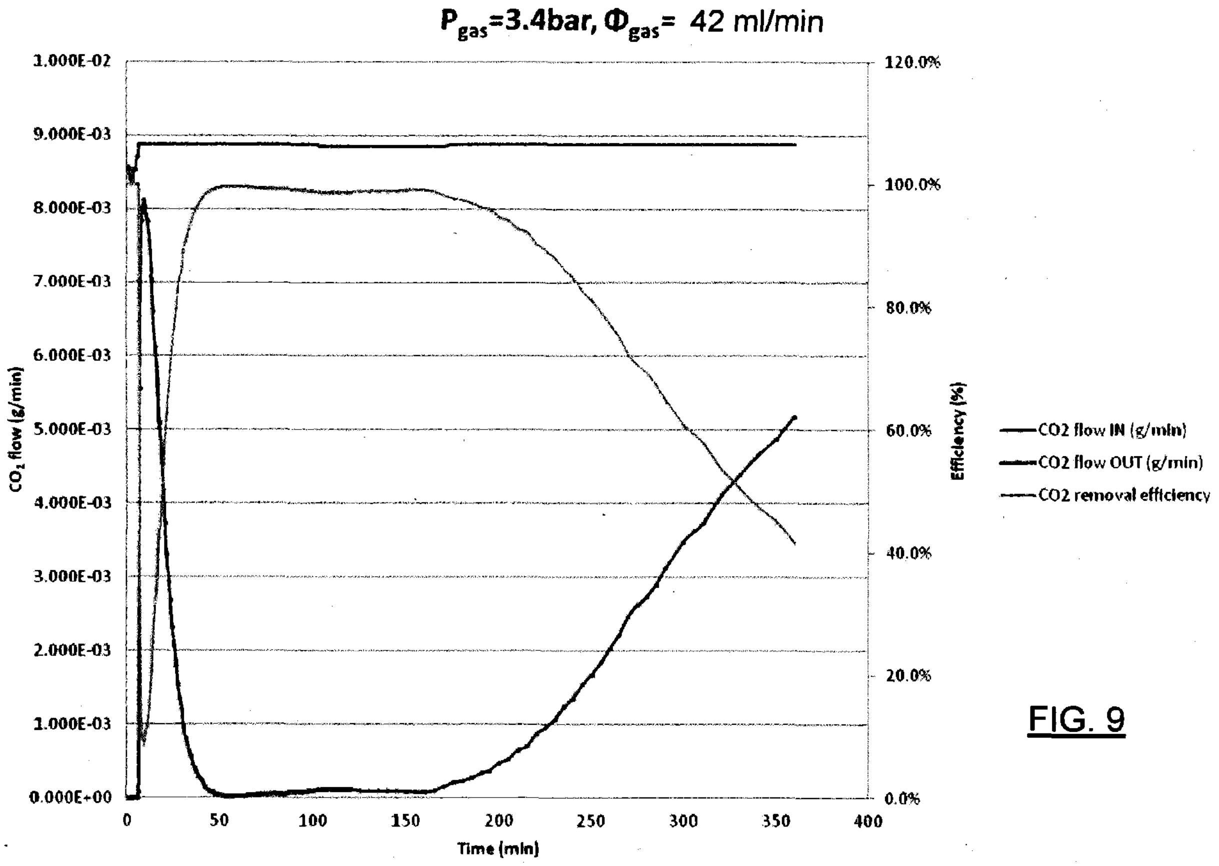

P_{gas}=3.4bar, Φ_{gas}= 42 ml/min
CO₂ flow (g/min)
1.000E-02
9.000E-03
8.000E-03
7.000E-03
6.000E-03
5.000E-03
4.000E-03
3.000E-03
2.000E-03
1.000E-03
0.000E+00
Efficiency (%)
120.0%
100.0%
80.0%
60.0%
40.0%
20.0%
0.0%
0
50
100
150
200
250
300
350
400
Time (min)
CO2 flow IN (g/min)
CO2 flow OUT (g/min)
CO2 removal efficiency

FIG. 9

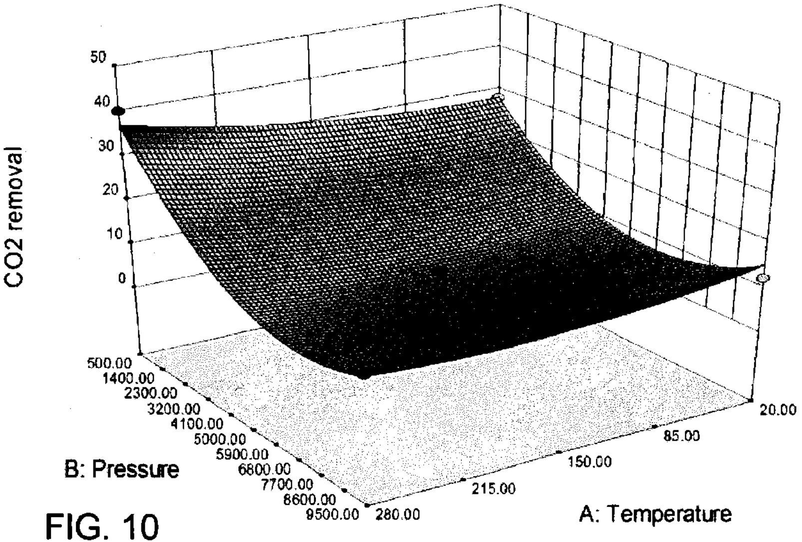

50
40
30
20
10
0
CO2 removal
500.00
1400.00
2300.00
3200.00
4100.00
5000.00
5900.00
6800.00
7700.00
8600.00
9500.00
B: Pressure
280.00
215.00
150.00
85.00
20.00
A: Temperature

FIG. 10

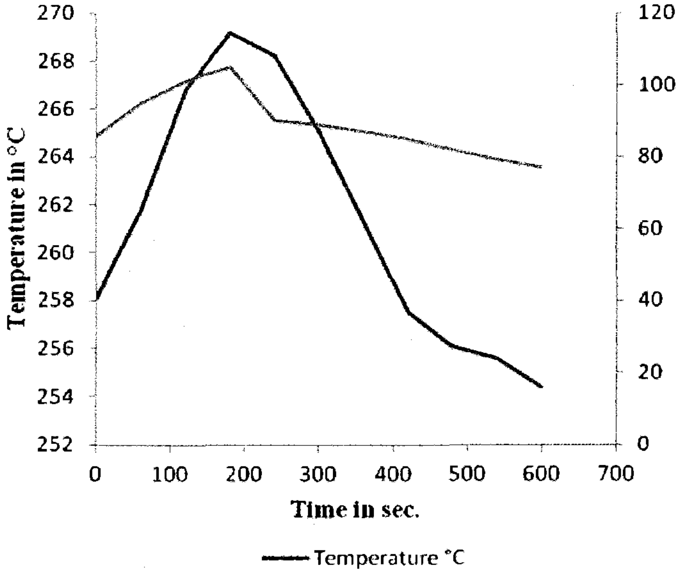

270
268
266
264
262
260
258
256
254
252
Temperature in °C
120
100
80
60
40
20
0
Pressure in psi
0
100
200
300
400
500
600
700
Time in sec.
Temperature °C

FIG. 11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050170

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***B01D 53/62*** (2006.01) , ***B01D 53/14*** (2006.01)
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: ***B01D 53/62*** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
EPOQUE, Canadian Patent Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 7 731 921 B2, Geerlings et al., 8 June 2010 (08-07-2010) *the entire document*	1-38 and 45-47
X	DE 196 22 292 A1, Edlinger et al., 5 December 1996 (05-12-1996) *the entire document*	1-38 and 45-47
Y	O'Connor, W.K., Dahlin, D.C., Rush, G.E., Gerdemann, S.J., Penner, L.R. and Nilsen, D.N., 2005. "Aqueous Mineral Carbonation - Mineral Availability, Pre-treatment, Reaction Parametrics and Process Studies-Final Report", DOE/ARC-TR-04-002, Albany Research Center, US DOE, pages 1-19.	1-38 and 45-47

[ ] Further documents are listed in the continuation of Box C. [X] See patent family annex.

*	Special categories of cited documents :	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report 04 June 2013 (04-06-2013)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer James McCarthy (819) 994-0411

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2013/050170

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. [ ] Claim Nos. :
because they relate to subject matter not required to be searched by this Authority, namely :

2. [ ] Claim Nos. :
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

3. [ ] Claim Nos. :
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows :

The claims must be limited to one inventive concept as set out in Rule 13 of the PCT. Where a group of inventions is claimed in one and the same international application, the requirement of unity of invention shall be fulfilled only when there is a technical relationship among those inventions involving one or more of the same or corresponding special technical features. The expression "special technical features" shall mean those technical features that define a contribution which each of the claimed inventions, considered as a whole, makes over the prior art. The independent claims of the present application are linked solely in the concept of carbon dioxide sequestration by carbonation of an alkaline earth metal, which is known in the art (see the background art cited in the application, for example). Accordingly, the claims are not considered to satisfy the requirements of Rule 13 of the PCT.

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :

4. [X] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. : 1-38 and 45-47

Remark on Protest [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

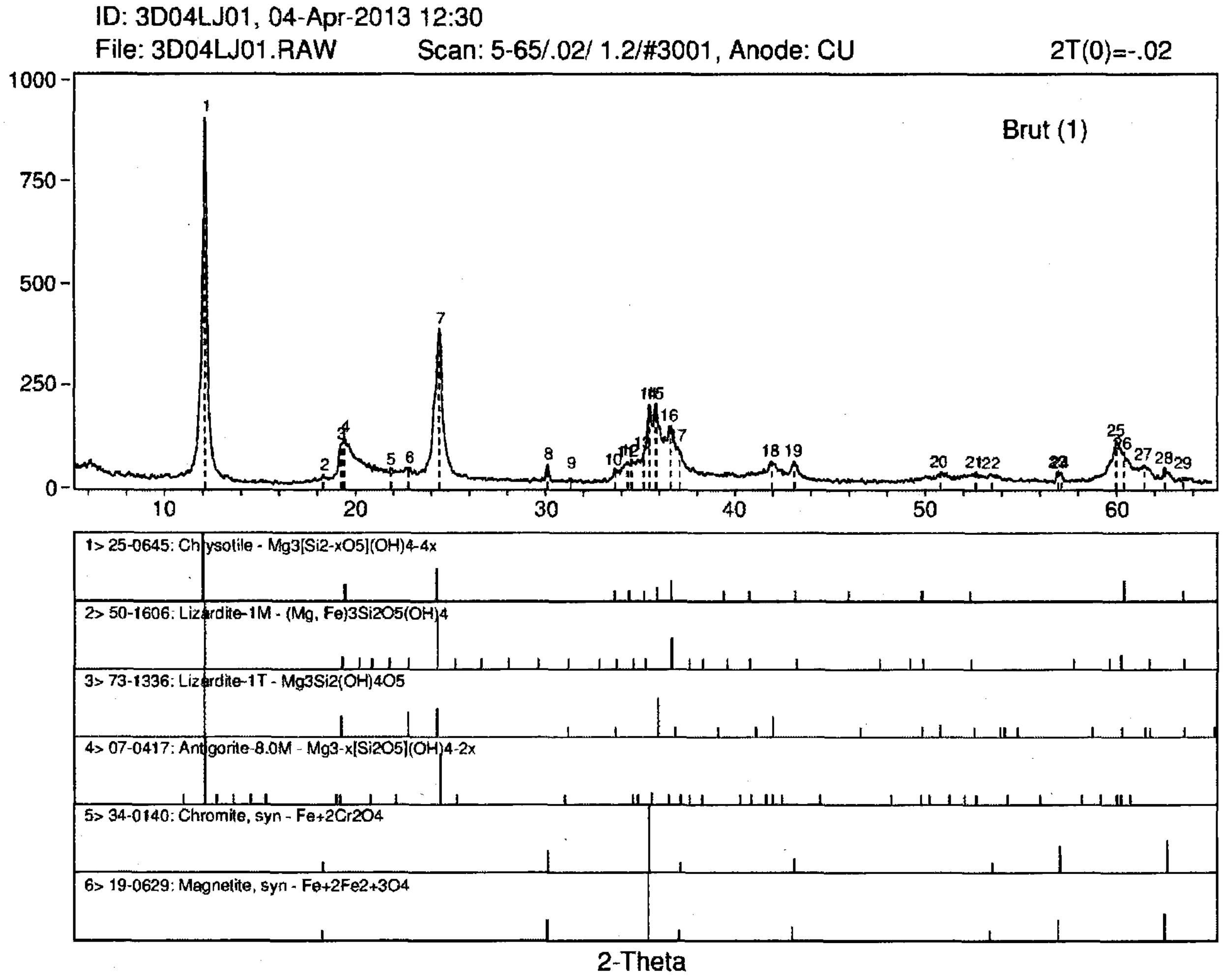
INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2013/050170

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
US7721921B2	25 May 2010 (25-05-2010)	CN1953932A CN1953932B DE202005020719U1 EP1753693A1 JP2007537101A JP4990130B2 US2008023501A1 WO2005110912A1	25 April 2007 (25-04-2007) 09 March 2011 (09-03-2011) 29 June 2006 (29-06-2006) 21 February 2007 (21-02-2007) 20 December 2007 (20-12-2007) 01 August 2012 (01-08-2012) 31 January 2008 (31-01-2008) 24 November 2005 (24-11-2005)
DE19622292A1	05 December 1996 (05-12-1996)	None	

ANNEXES

Annexe 1 : Diffractogramme du résidu brut



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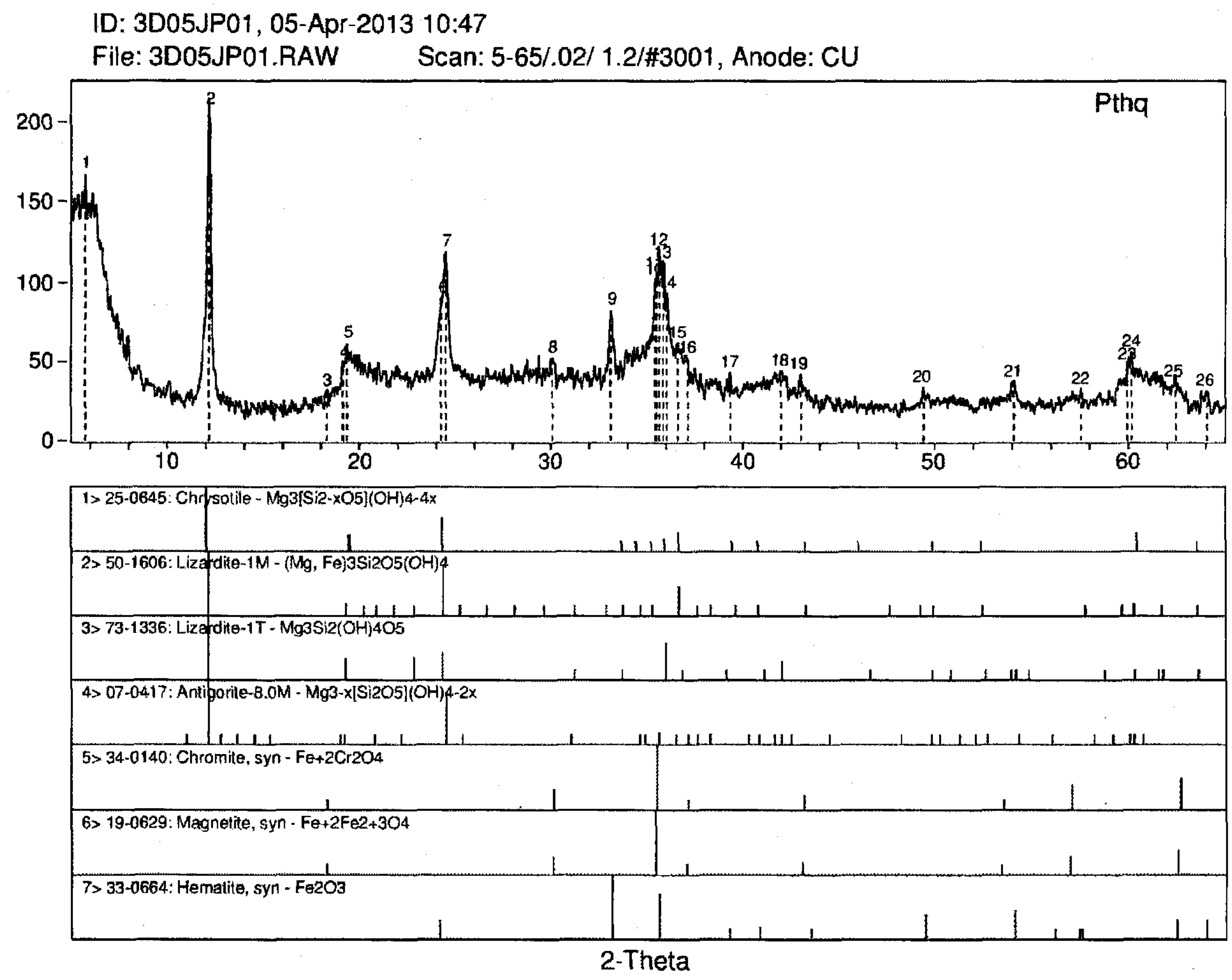
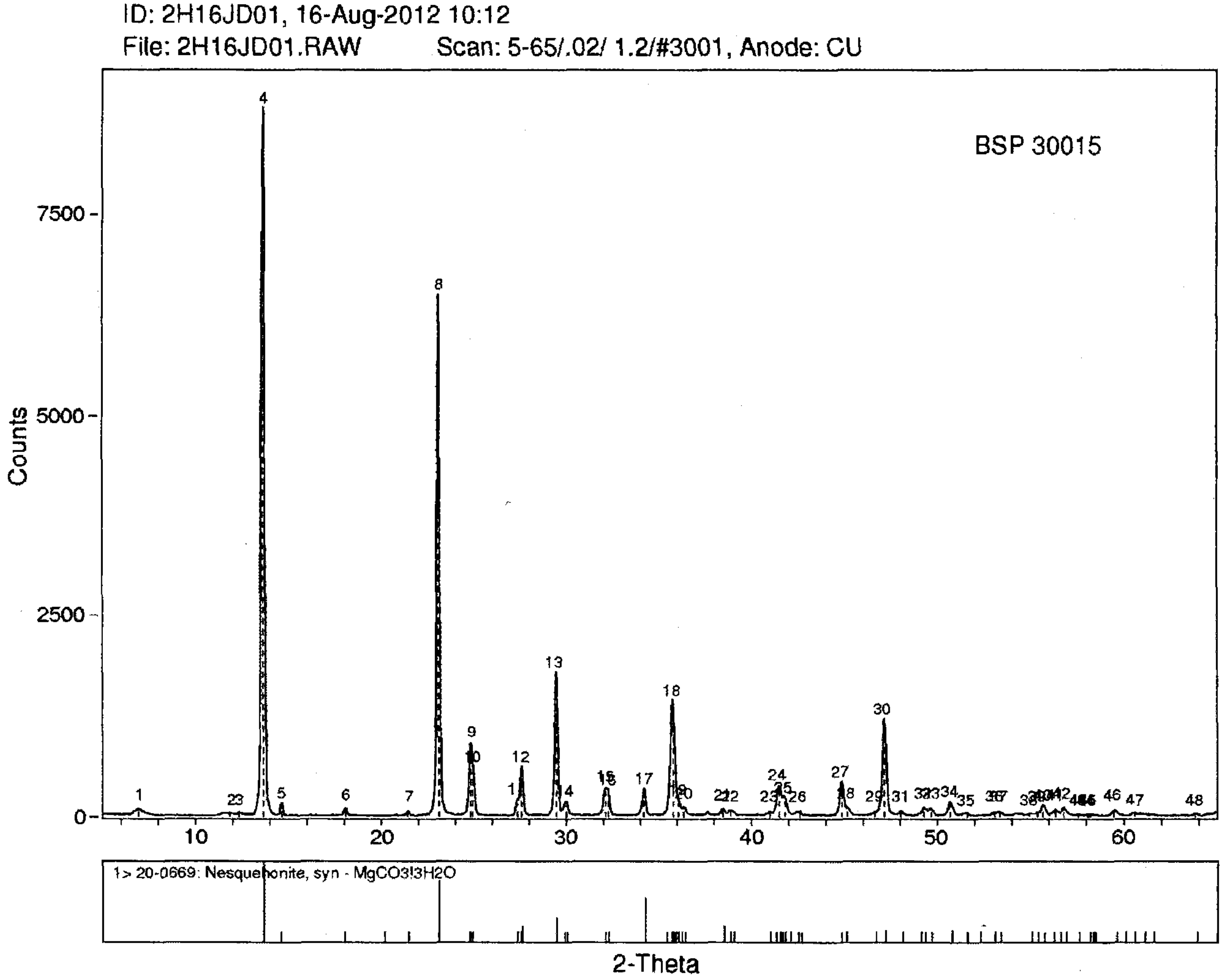
Annexe 2 : Diffractogramme du résidu après activation thermique



Universite Laval,Quebec. - Thu Apr 11 2013 @9:41am

Annexe 3 : Diffractogramme du carbonate de magnésium



Universite Laval,Quebec. - Thu Aug 16 2012 @11:15am