HYDROMETALLURGICAL RECOVERY OF ZINC, MANGANESE AND LEAD FROM PYROMETALLURGY SLUDGE

*J. Mocellin[1,2,3], M.-O. Simonnot[1], G. Mercier[2], J.-F.Blais[2], J.-L. Morel[3]

[1] *Laboratoire Réactions et Génie des Procédés, Université de Lorraine CNRS*
1 rue Grandville BP 20451
Nancy, France Cedex 54001
*(*Corresponding author: julien.mocellin@ete.inrs.ca)*

[2] *Institut National de la Recherche scientifique, INRS*
490 rue de la Couronne
Québec, (Québec) Canada G1K 9A9

[3]*Laboratoire des Sols et Environnement, Université de Lorraine INRA*
TSA 40602, 2 avenue de la Forêt de Haye
Vandoeuvre lès Nancy, France 54618

ABSTRACT

Large quantities of ferromanganese sludge are generated as waste material by blast furnace during the manufacturing of ferromanganese. These slags are very rich in manganese, zinc and lead (5 to 40 %). These residues have been deposited in a pond in periphery of the steel industry. Considering the market value of the metals, these brownfield sites can now be considered as secondary resources. We have developed a hydrometallurgical process for selectively leaching Zn, Mn and Pb in order to produce compounds of Mn and Zn pure enough to be economically recoverable and a residue rich in Pb. Batch laboratory experiments were carried out to determine appropriate leaching conditions to maximize zinc extraction (100 %) and manganese extraction (90.0 %) with sulfuric acid and to generate a residue containing 15 to 30% of lead. This Pb residue is recyclable by another process.

KEYWORDS

Manganese, zinc, lead, hydrometallurgy, recovery, ferromanganese, residue

INTRODUCTION

Pyrometallurgical industries traditionally based in northern and eastern France have generated wastes with a high concentration of Mn, Zn and Pb (5 to 40%). Those residues were produced during the processing of wet scrubber residue of offgas stream and were deposited next to the blast furnace. No practical method is known to decontaminate these residues and recover Mn, Zn and Pb. Over the past century, the industry did not encourage the recovery of those metals as the metal price was low and the environmental regulation not as strong as now. Currently the metal market has a high price level and these industrial sites can be considered as secondary resources (Huot, Faure, Biache, Lorgeoux, Simonnot, & Morel, 2014; Huot, Simonnot, Marion, Yvon, De Donato, & Morel, 2013; Huot, Simonnot, Watteau, Marion, Yvon, De Donato, & Morel, 2014). The aim of the project is to develop a commercially viable process with capability to produce compounds of Mn, Pb and Zn pure enough to be recoverable. The originality of the project is to develop an hydrometallurgical process that will selectively leach Zn, Mn and Pb in order to obtain a concentrate of Zn, a concentrate of Mn and a residue rich in Pb. The aim of this article is to present the hydrometallurgical process with some examples. A flow sheet of the process is given in Figure 1.

Zinc is a natural and completely recyclable element used in different industries (chemical, textile and metallurgical industries). Although historically extracted from sulfides, Zn is now increasingly extracted from secondary sources such as electric furnace residues. Zn is recovered by pyrometallurgical and hydrometallurgical processes from ores or secondary sources. So far, pyrometallurgical processes for producing Zn metal consume too much energy and are too costly. Hydrometallurgical processes will be preferred as they are often less costly while being environmental friendly (Jha, Kumar, & Singh, 2001). In most studies, Zn has been leached with NaOH (Charpentier, Rizet, & Trouillet, 2007), NH_4Cl (Olper, Fracchia, & Maccagni, 1993) or H_2SO_4 (Acharya, Ghosh, Anand, & Das, 1999; Dvorak & Jandova, 2005; Shawabkeh, 2010).

Manganese is used as an additive in steel manufacture to improve steel strength; it is also necessary to chemical industry for the production of batteries and fertilizers. The main sources of manganese are as an oxide in pyrolusite (MnO_2) and braunite ($3Mn_2O_3.MnSiO_3$) (Fisher, 2000). MnO_2 is insoluble in dilute H_2SO_4 solution but when reduced to MnO, it readily dissolves to give a solution of $MnSO_4$ (Habashi, 1969; Naik, Sukla, & Das, 2000). Mn(IV) is usually leached with sulfuric acid using a reducing agent, such as sulfuric acid leaching coupled with hydrogene peroxide (Allen & Corwin, 1989; Jiang, Yang, Huang, Zhang, & Qiu, 2004), ferrous sulfate (Brantley & Rampacek, 1968; Das, Sahoo, & Rao, 1982; Vu, Jandova, Lisa, & Vranka, 2005), oxalic acid (Sahoo, Naik, & Das, 2001), sulfur dioxide (Abbruzzese, 1990; Acharya et al., 1999; Chow, Nacu, Warkentin, Aksenov, & Teh, 2012; Ward, 2005a, 2005c). Some studies have shown the reducing properties of agricultural wastes such as saw residue (Hariprasad, Dash, Ghosh, & Anand, 2007), lactose (Veglio, Volpe, Trifoni, & Toro, 2000), glucose (Furlani, Pagnanelli, & Toro, 2006; Pagnanelli, Garavinia, Veglio, & Toro, 2004), molasses (Lasheen, El Hazek, & Helal, 2009; Su, Wen, Wang, Sun, & Tong, 2008), corn cobs (Tian, Wen, Yang, Liang, Pi, & Wang, 2010).

Sodium metabisulfite ($Na_2S_2O_5$) (Owusu & Gertenbach, 2009) has also been studied as substitute for SO_2 gas in the leaching process to reduce MnO_2 (Equation 1). $Na_2S_2O_5$ will be used as the reducing agent in this study.

$$2MnO_2 + H_2SO_4 + Na_2S_2O_5 \rightarrow 2Mn^{2+} + H_2O + 3SO_4^{2-} + 2Na^{+} \quad (1)$$

In most extractive metallurgy processes, metals are leached simultaneously. The leachate contains impurities and further purification of the solution is often required. Precipitation of metals as hydroxides or sulfides are purification techniques used to remove unwanted metals (Zhang & Cheng, 2007). The purpose is to precipitate metals like Fe, Al and Si in a first step while keeping Zn and Mn in solution at chemical costs as low as possible. In a second and a third step, Mn compound and Zn compound are precipitated. We propose a quite different strategy. The approach consists in selectively solubilizing Zn, obtaining a first leachate and, after solid liquid separation, Mn is solubilized from the solid already depleted in Zn. The number of purification steps will be decreased and the process simplified. After solubilization of Zn and Mn, Zn is precipitated by adding Na_2S to produce ZnS and Mn as $MnCO_3$ by adding Na_2CO_3. Zn could also be electrodeposited (after oxidation) or precipitated as $Zn(OH)_2$.

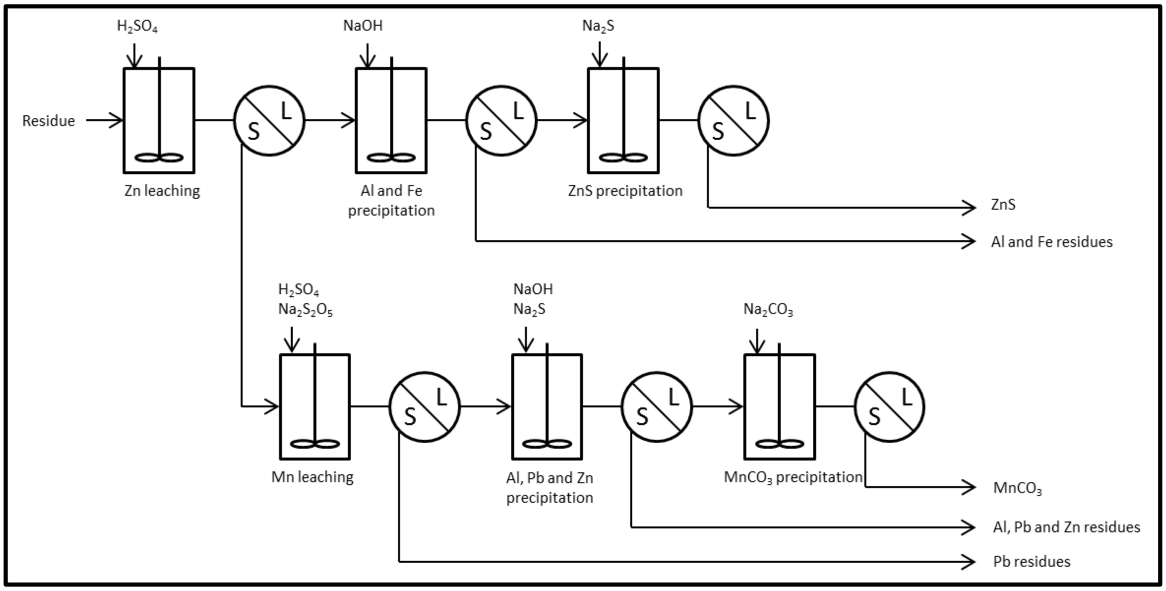

Figure 1 – Flow sheet of the process

MATERIALS AND METHODS

Materials

The residues were obtained from a former settling pond of the iron industry of Lorraine (Northeast France), which was in service from 1875 to 1986 (Huot, Faure, et al., 2014; Huot et al., 2013; Huot, Simonnot, et al., 2014). This site was situated close to the Moselle and Meurthe rivers and has been colonized by vegetation (Figure 2a). The pond was separated in several layers which had widely different chemical compositions (Table 1). The Figure 2b presents a photograph profile of different layers in the settling pond. Elemental composition was dominated by Mn, Ca, Si, Fe, C, Zn, Pb and Al. Mn content reached up to 341 g/kg of dry soil. Layer 16 will be used for this study because it had a high concentration in Mn, Pb and Zn which is representative of the average concentration in the soil. The composition of some different layers are shown in Table 1.

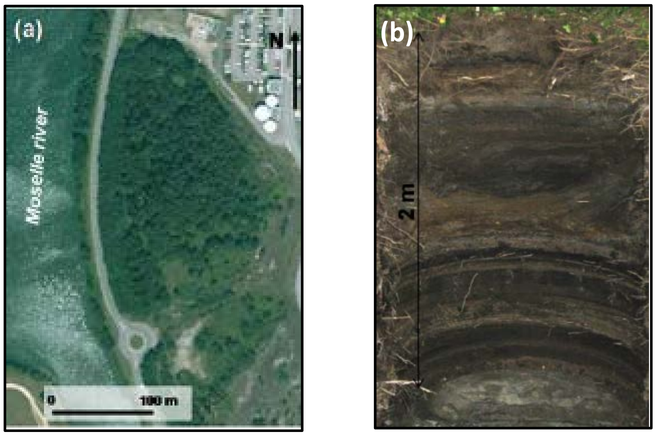

Figure 2 – Aerial view of the studies settling pond (a) and profile of different layers in this pond (b) (Huot, 2013; Huot et al., 2013).

Table 1 – Element concentration in the metallic residue (g/kg)

	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
Layer 16	198.0	72.9	45.3	72.0	56.3	52.3	11.5	13.1	18.7	3.2
Layer 19	29.7	28.5	62.3	16.7	151.3	18.6	13.9	5.9	43.2	5.1
Layer 11	0.3	0.5	0.4	0.0	2.2	0.4	0.0	4.8	0.3	1.6
Layer 9	252.5	4.3	51.7	6.1	53.7	12.1	13.4	5.4	8.0	1.9

Leaching experiments

All the leaching experiments were performed in an agitated batch reactor with baffles (Figure 2a). About 400 g of the pyrometallurgical residue (Table 1) were mixed three times with sulfuric acid solution at 0.25 mol/L, at a solid/liquid ratio of 10. The residue was rinsed three times to leach Zn. The reactor content was agitated continuously at 700 rpm .In the second part of the process, the residue was leached twice in a second solution with sulfuric acid and sodium metabisulfite as a reductant to leach Mn. After leaching, the solid/liquid mixture was centrifuged for 10 min at 1500 rpm (Allerga^{TM}6 Centrifuge, 60 Hz, 120 V, Series By Beckman Coulter^{TM}, U.S.A.). The slurry was filtered by vacuum filtration on a Whatmann 934-AH glass microfiber filter (pore size= 1.5 μm). The solid residue was dried overnight in an oven at 90 °C until constant weight. The residue and the filtered slurry were then analysed by ICP-AES (Varian, model Vista-AX simultaneous ICP-AES) after *aqua regia* digestion, according to the CEAEQ method (MA. 205-Met/P 1.0). Analysis was controlled using reference certified solutions obtained from SCP Science, and Rhenium and Rhodium were used as internal standards.

Leachate purification and metal precipitation

Precipitation tests were performed within a 1 L glass beaker with 1 L of leach liquor (Figure 3b). The tests have been performed in triplicate for the first three steps of Zn leaching (L1, L2 and L3 Zn Table 2). Leach liquor pH was adjusted to about 4.50 - 4.75 to precipitate silicate, iron and aluminum by sodium hydroxide addition as an alkaline agent. The solution was settled 2 hours until the suspended matter has decanted. After decantation, the purified leachate was collected and the residue centrifuged to recover pore water. Then the purified leachate and residues were analyzed. Zn was then precipitated in triplicate from the purified leachate using Na_2S as a precipitation agent. Precipitation was run in a beaker with twice the stoichiometry (considering the concentration of Zn) of Na_2S. The solid residue was centrifuged and dried overnight in a fumehood before analysis. Before Mn precipitation, leaching liquor were purified in triplicate at pH between 5.2 and 5.6 with 10 times the stoichiometry (considering the concentration of Zn) of Na_2S. This step was used to remove Zn, Pb and Al in solution. Then manganese carbonate was precipitated in triplicate, one set of three identical precipitation, from 1 L of the corresponding leachate, L1 and L2 Mn (Table2),using stoichiometry of Na_2CO_3 as a precipitation agent (considering the concentration of Mn) then Na_2CO_3 was added until pH 8.5 to complete $MnCO_3$ precipitation. This precipitation is very fast at ambient temperature (Figure 3d). Afterwards, the suspension was filtered, the formed cake was re-pulped and washed with pure water and filtered again to remove impurities from the cake of $MnCO_3$ (Figure 3f). Manganese carbonate and zinc sulfide were solubilized with *aqua regia* before analysis by ICP-AES.

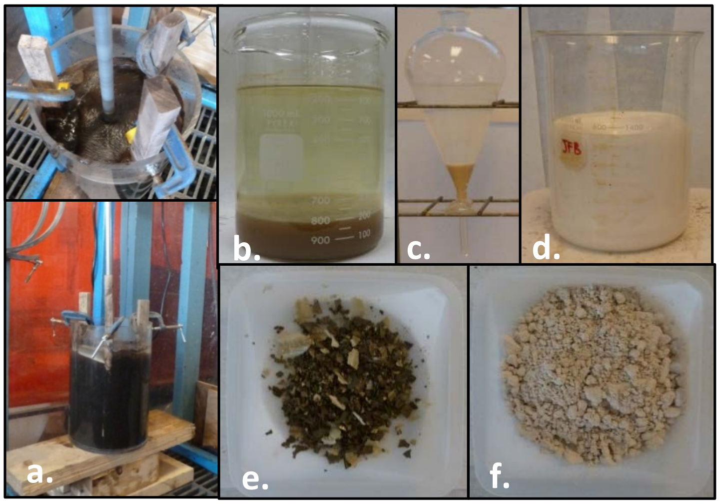

Figure 3 – Photographs at different stages of the process

RESULTS AND DISCUSSION

In the first leaching step, about 97.6 % of Zn and 12.5 % of Mn have been extracted from the residue at pH between 1.70 and 3.63. The element concentrations in the leachate are listed in Table 2. These results show that Mn, mainly in the form of MnO_2, was not leached in the absence of a reducing agent. Zn was preferentially leached in the first leaching step and, to a lesser extent, MnO. The crystallographic characterization (X-ray diffraction, IR spectroscopy, SEM/EDS and TEM/EDS) of residues has been realized on previous work (Huot, 2013). These preliminary works show in this residue Zn was mainly associated with aluminosilicate and Mn oxides; therefore it was easily leachable in acid at 20 °C. For this reason, it is not necessary to use a high temperature and high concentration of acid to improve Zn extraction (Leclerc, Meux, & Lecuire, 2003; Trung, Kukurugya, Takacova, Orac, Laubertova, Miskufova, & Havlik, 2011). In the second leaching step (L1, L2, R1 and R2 Mn Table 2), 90.0 % of the Mn was leached. At the same time, only 1.0 to 3.0 mg/L of Fe and Al were leached at pH between 3.94 and 4.64. The Mn concentration reached 10 g/L in the first leachate (L1 Mn), for only 7.83 mg/L of Pb, 1.06 mg/L of Al and 1.77 mg/L of Fe. pH control by addition of sulfuric acid during Mn leaching is very important. pH must be strictly fixed to leach Mn without solubilizing Fe and Al, to avoid purification steps and to be able to precipitate Mn more easily (cheaper) afterwards. The weight of dry residue after leaching was 177.5 g. This final residue contained 14.8 % Pb which was insoluble in sulfuric acid but can be recovered by pyrometallurgical processes (contact with a recycling company). This residue has lost about 55.6 % of its original mass and it significantly reduced the quantity of waste to be treated. The element concentrations in the metallic residue after the process are presented in Table 3.

Table 2 – Elements concentration in the various leachates residue (mg/L)

	Volume (mL)	pH	Mn	Pb	Al	K	Ca	Fe	Zn
L1 Zn	2910	3.63	386	4.49	390	370	506	5.30	421
L2 Zn	4140	2.67	866	7.70	1566	249	495	61.9	754
L3 Zn	4160	1.70	780	7.58	1093	118	557	917	469
R1 Zn	4020	2.00	294	4.84	408	47.9	522	193	166
R2 Zn	4000	2.28	117	4.46	141	22.0	538	29.5	54.9
R3 Zn	4000	2.49	64.6	3.93	87.6	14.7	544	4.60	28.5
Extraction (%)			12.5	0.44	81.2	10.2	54.5	23.9	97.6
L1Mn	2850	4.64	10194	7.83	1.06	25.0	542	1.77	31.4
L2 Mn	2700	3.94	8148	5.03	2.60	12.7	548	2.69	55.9
R1 Mn	2550	4.25	2813	4.67	1.41	6.64	503	1.80	23.6
R2 Mn	2550	4.62	1233	4.39	0.88	7.55	516	1.35	16.7
Extraction (%)			90.0	0.6	81.3	10.7	79.5	24.0	100

Table 3 – Element concentration in the residue after the process (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
47.7	148	14.8	0.0	27.8	81.3	0.0	26.2	1.60	52.9

Leaching liquor purification

Leachate purification was performed using a precipitation technique. The aim of precipitation is to remove Fe and Al from the leachate after Zn leaching step (L1, L2 and L3 Zn Table 2). The element concentrations in the leachate and in the purified leachate are presented in Table 4. The major parts of Fe and Al have been precipitated without Zn and Mn. Al and Zn elimination can be improved by a slight increase in pH. Previous experiments had shown at a pH of 5.00 for L2 Zn, the Al and Fe are totally removed but 25 % of Zn and 10 % of Mn have also been eliminated. .

Table 4 – Element concentration in the leachate before and after purification (mg/L)

	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S
L1 Zn Before	3.63	386	4.50	390	370	506	5.30	437	421	2269
L1 Zn After	4.75	376	3.58	36.7	364	494	3.88	436	414	2191
L2 Zn Before	2.67	866	7.70	1566	249	495	61.9	336	754	4874
L2 Zn After	4.75	791	2.89	57.4	230	464	2.49	316	707	4220
L3 Zn Before	1.70	780	7.60	1093	118	557	917	178	469	6404
L3 Zn After	4.75	670	1.63	37.6	101	497	2.48	160	414	5472

Zinc precipitation

In this test, around 800 mL of L1, L2 and L3 Zn after purification solution (Table 4) were precipitated with Na_2S (Figure 3c). Table 5 shows that most of Zn has been precipitated with sulfides to form ZnS (Figure 3e) while Mn did not precipitate; it will be precipitated as carbonate in a further stage. This step is not considered in this study. The low Zn concentration and the presence of Pb, Al and Mn in the same concentration range are a major problem in this step to recover Zn without impurities. The results of Zn precipitation are shown in Table 6. Zn concentration in the precipitate is between 52.6% and 66.0%. For the leach solution L1 and L2 Mn, Na_2S is used to precipitate Al, Pb and Zn in solutions which are considered like impurities for Mn precipitation.

Table 5 – Element concentration leachate before and after the precipitation (mg/L) during precipitation as Zn sulfide

	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S
L1 Zn Before	4.32	376	3.58	36.7	364	494	3.88	436	414	2191
L1 Zn After	4.54	364	0.93	34.3	368	484	0.00	424	2.03	2102
L2 Zn Before	4.36	791	2.89	57.4	230	464	2.49	316	707	4220
L2 Zn After	4.59	738	0.75	57.2	230	445	0.00	300	1.16	3940
L3 Zn Before	4.54	670	1.63	37.6	101	497	2.48	160	414	5472
L3 Zn After	4.74	637	0.55	36.2	105	478	0.00	152	0.92	5094
L1 Mn Before	4.48	10194	7.83	1.06	25.0	542	1.77	39.9	31.4	14441
L1 Mn After	7.23	10125	2.11	0.14	23.4	544	1.08	39.0	0.57	13887
L2 Mn Before	3.52	8148	5.03	2.60	12.7	548	2.69	42.4	55.9	12414
L2 Mn After	7.33	7499	1.70	0.18	13.8	517	0.59	39.0	0.35	11279

Table 6 – Element concentrations (g/kg) in ZnS precipitate

	Mn	Pb	Al	K	Ca	Fe	Mg	Na	Zn	**ZnS**
L1 ZnS	11.1	3.02	4.60	6.49	6.21	2.40	5.91	15.6	443	**660**
L2 ZnS	19.3	1.33	3.96	3.54	4.88	0.64	3.63	44.9	400	**596**
L3 ZnS	13.2	0.81	3.80	1.52	7.01	0.41	1.79	71.6	354	**527**

Manganese precipitation

The leaching liquor L1 and L2 Mn have been purified before Mn precipitation, the majority of Zn, Pb and Al has been removed (Table 5). In this step, around 1 L of leach liquor (L1 Mn After) with a Mn concentration of 10125 mg Mn/L was precipitated with 21.8 g of Na_2CO_3; for L2 a Mn concentration of 7499 mg Mn/L was precipitated with 16.2 g of Na_2CO_3 (Figure 3d). After precipitation, the solid manganese carbonate was separated from the solution by filtration on a Fisher Scientific filter paper P8-Creped Cat No:09-790-12g Dia 18.5 cm (Figure 3f). The filtered manganese carbonate cake was then rinsed with pure water and separated by another filtration. The rinsing step enabled us to remove the major impurities like Na and S present in the cake. The results before and after rinsing are shown in Table 7. The Mn concentrations in the cake were 45.7 % for L1 and 43.2 % for L2 after two rinsing steps. The major impurities in the cake are respectively Ca, Na and S.

Table 7 – Element concentrations (g/kg) in the final cake before and after rising

	Mn	Pb	Al	K	Ca	Fe	Mg	Na	Zn	S	**$MnCO_3$**
L1$MnCO_3$ Before	396	0.00	0.08	0.00	12.1	0.12	0.53	24.6	0.02	14.5	**829**
L1MnCO3 After	453	0.00	0.00	0.00	13.8	0.36	0.00	12.4	0.03	1.79	**948**
L2$MnCO_3$ Before	389	0.00	1.10	0.00	35.5	1.48	0.53	23.6	0.98	32.0	**814**
L2$MnCO_3$ After	432	0.00	0.62	0.00	33.6	2.10	0.00	5.14	0.89	10.2	**903**

CONCLUSION

This article shows a part of the performance of this hydrometallurgical process to recover Zn, Mn and create a residue enriched in Pb from pyrometallurgical residue containing high concentration of Mn, Zn and Pb. The control of chemical conditions (pH)) allows a leaching of Zn and Mn with minimal impurities. The recovery rates reached 100 % for Zn and 90.0 % for Mn. The leaching solution contained 754 mg/L of Zn and 10125 mg/L of Mn. It was then purified to form high-value precipitates of ZnS or $MnCO_3$ with a fairly acceptable concentration of impurities. It was therefore possible to create a precipitate of $MnCO_3$ with 45.3 % of Mn with a low concentration of impurities like Na, S, Zn and Pb. $MnCO_3$ is currently sold with a purity of at least 44-46 % of Mn. Theoretically, the highest degree of purity in the $MnCO_3$ is 47.8 % of Mn. The aim of this process is to be applicable and effective to other residues with various concentrations of Zn, Mn and Pb.

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