Original Research Paper

Recovery of Manganese from Zinc Smelter Slag

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Abstract: Using a software-based experiment design, the application of the leaching process for the extraction of manganese from Zinc Plant Slag (ZPS) was investigated. In this study, the effect of different parameters, i.e., H_2SO_4 concentration, pulp density, agitation rate, temperature and reaction time, was investigated. Response Surface Methodology (RSM) based on the Central Composite Design (CCD) has been implemented to consider the main parameters. A hydrometallurgical route to manganese silicate from spent zinc plant residue has been proposed in this investigation. Based on the investigation, Mn can be extracted from ZPS in sulfuric acid without any oxidant agents. The results showed that the optimum conditions of this study are an H_2SO_4 concentration of 2 mol/L and a solid/liquid ratio of 0.07 g/mL at 50°C for 150 min and an agitation speed of 1000 rpm. A manganese leaching efficiency higher than 83% is reached under these conditions, with a corresponding 22% iron, 23% lead, 68% zinc and 65% aluminum.

Keywords: Manganese, Zinc, Acid Leaching, Slag, Precipitation

Introduction

Manganese is one of the most widely used metals in the world, ranking fourth after iron, aluminum and copper (Charef *et al*., 2017), which is used in various fields including steel production, batteries, nonferrous metallurgy and fine chemicals (Aksoy and Sagol, 2016; Alaoui *et al*., 2016). In steelmaking processes either indirectly through ferroalloys production or directly in pig iron, manganese has a substantial role that cannot be substituted with any other compound. For a long time, the unequal distribution of global manganese resources has been acknowledged as a problem for the United States and other industrialized countries with insufficient domestic resources to supply their markets. Consequently, it would be advantageous to look for more available sources of manganese to support the supply of this commodity in the event of future supply disruptions (Schulz *et al*., 2018).

The continuous loss of natural resources, increasing energy prices and tight environmental restrictions also lead to expanded metal recovery efforts (Ghosh *et al*., 2016; Shen *et al*., 2007; Xin *et al*., 2011). The development of a competent and cost-effective extractive method is now awaiting low-grade ores in millions of tons (Ghosh *et al*., 2016; Pradhan *et al*., 2006) (Arsent'ev *et al*., 1991). High-grade manganese ore resources (>40%) are

typically used to produce metallic alloys by pyrometallurgical processes as they are more readily available for this process (Aslan, 2007). Moreover, hydrometallurgical methods have also been introduced widely to extract Mn from low-grade ores, residuals and other secondary sources. There are several reports on leaching of low-grade manganese from carbonate and silicate ores, which mainly include direct acid leaching, pre-roasting followed by acid or water leaching, reductive acid leaching and electrochemical leaching. To recover manganese from the aforementioned manganese minerals, several acid leaching processes have been developed (Arsent'ev *et al*., 1991; Ghassa *et al*. 2017; Genuino *et al*., 2018). Comba *et al*. (1991) proposed an efficient leaching method for manganese-bearing silicates ($MnSiO_3$ and $[(Mn,Fe)SiO_3]$ as major phases) using HCl and CaF_2. Where a countercurrent leaching procedure was introduced to extract Mn along with CaF_2 (99%) as a by-product. In another study, Mn leaching recovery of above 90% with sulfuric acid (80 wt.%) in 90 min was reported (Charef *et al*., 2017).

In the case of common-occurring manganese oxide mineral (e.g., MnO_2), Mn of higher oxidation state, i.e., Mn (IV), must first be reduced to MnO, which then can be leached in a dilute acid solution (Li *et al*., 2017). Two methods have been suggested for this purpose:

1) Hydro reduction in the presence of various chemical reducing agents (Lin *et al*., 2016; Mohanty *et al*., 2017; Reuter *et al*., 2004)
2) Pyro-reduction at high temperature (Wasserstein and Lazar, 2016)

Slags are generated in various pyrometallurgical processes, including pretreatments in metals extraction, refining and alloying, which usually consist of a combination of oxides, sulfides, elemental metals and silicate minerals. During these processes, huge amounts of slags are generally produced and disposed of to process tailings. Due to their metal content, slags also are of great environmental concern, control of which imposes an extra cost to the process. Recycling of the by-product slags is an attractive alternative for reducing or eliminating the disposal costs and environmental drawbacks, which to some extent, saves resources as well. Based on the origin and properties of the slags, recycling techniques are classified for three main slag categories, i.e., ferrous, nonferrous and incineration (Chandra *et al*., 2011; Chen *et al*., 2017). Zinc slag, which is produced in zinc roasting plants, can be considered as a valuable secondary source for Mn recovery. While landfill disposal of this waste can have a detrimental impact on the environment due to the high concentration of heavy metals, proper recovery of these elements from zinc slag can provide economic benefits. Zinc sulfide mineral (sphalerite) is one of the most important commodities for Zn production. More than 80% of zinc is produced by hydrometallurgical treatment of ZnS in the Roast-Leach-Electrowinning (RLE) process (Xue *et al*., 2016). Sphalerite should be roasted at high temperatures (up to 1100°C) in the presence of carbon to produce acid-soluble Zinc calcine (ZnO) following the reaction (1) (Cai *et al*., 2013):

$$2ZnS + 3O_2 = 2ZnO + 2SO_2 + \Delta H \qquad (1)$$

At this temperature during roasting, slag will be formed, which contains an elevated concentration of light metals (such as silicon, iron, manganese, calcium and aluminum) in various forms. Manganese is one of the most important metals enriched in zinc slag.

In this study, the effect of various parameters at different conditions on leaching recovery of Mn from zinc slag using sulfuric acid is investigated. The optimum leaching conditions and a mathematical model (based on central composite design methodology) for manganese extraction are presented and discussed in detail.

Materials and Methods

Slag Sample

The slag sample was obtained from a zinc-lead roasting plant, located in Yazd, Iran. After size reduction, the -20 mm sulfide minerals (mostly sphalerite and galena) are charged to a rotary kiln in the presence of coking coal. The mineral/coke ratio is fixed on 7/3 and minerals are roasted at 1100°C. The produced soluble calcine is then used for Zn production and the generated black slag is disposed of to the tailing dam. Representative samples were collected from the tailing to study the potential extraction of valuable metals. The fine particles fuse, making coarser slag particles during the roasting at elevated temperatures. Further size reduction consisting of jaw and cone crushers followed by a ball mill was used for grinding the slag sample to the particle size of below 75 μm. The chemical composition of the slag sample used in this study was determined by the X-Ray Fluorescence (XRF) and is given in Table 1 and Fig. 1.

The Atomic Absorption Spectroscopy (AAS) (Agilent VGA 77) analysis also indicated that the slag sample contains 10.47% manganese. In addition, Si, Fe, Al and Ca were found to be the primary constituents in their oxide forms. Moreover, XRD analysis revealed the patterns of tephroite (Mn_2SiO_4), fayalite (Fe_2SiO_4) and wurtzite (ZnS) in the sample. Quartz, dolomite, feldspar group (calcium and potassium groups) and an amorphous phase (perhaps the fused silicate) were also detected in the slag sample at varying but not major extents.

Acid Leaching

The leaching tests were carried out in a 500 mL glass reactor heated on a hot plate equipped with a digital controlled stirrer and a temperature regulation thermometer for various conditions on representative samples. The effect of five different parameters, including acid concentration, solid/liquid ratio of pulp, agitation rate, temperature and reaction time was investigated. The leaching solution was prepared using distilled water and the analytical grade H_2SO_4 at target concentrations. The amount of solution was calculated based on the desired solid/liquid ratio and first added to the system. When the solution reached the required temperature, 5 g of slag sample was added into the glass reactor and the pulp was stirred at a certain rate. After leaching, the Pregnant Leach Solution (PLS) was analyzed for its content of the elements of interest using the AAS analysis and Total Reflection X-Ray Fluorescence (TXRF) (GNR-TX2000, Italy). The metals recoveries were calculated according to Equation 2:

$$R = \frac{C_1 V}{C_0 m} \times 100 \qquad (2)$$

where, R is the metal recovery (%), C_1 is the Mn concentration in PLS (mg/l), V is the leachate volume, C_0 is the concentration of Mn in feed slag sample (mg/kg) and m is the mass of feed slag (kg) (Charef *et al*., 2017).
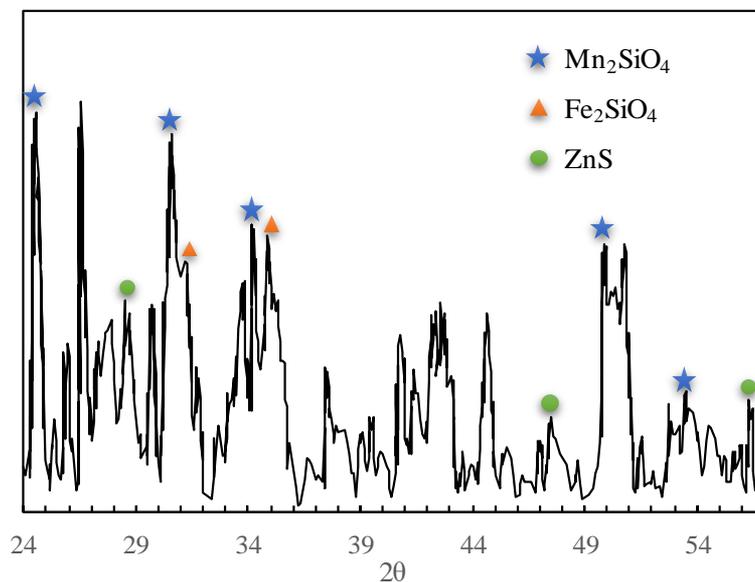
Fig. 1: XRD pattern of slag sample

Table 1: Chemical analysis of slag sample (mass fraction)

Composition	SiO_2	MnO	Fe_2O_3	Al_2O_3	CaO
Content (%)	29.92	13.52	17.77	9.67	16.44

Table 2: Independent variables and their levels for CCD

		Actual values and coded levels				
Independent variable		$-\alpha$	-1	0	+1	$+\alpha$
Sulfuric acid concentration (M)	A	0.50	1.00	1.50	2.00	2.50
Stirring speed (rpm)	B	400.00	600.00	800.00	1000.00	1200.00
Temperature (C)	C	40.00	50.00	60.00	70.00	80.00
Leching time (min)	D	60.00	90.00	120.00	150.00	180.00
Solid/Liquid ratio	E	0.01	0.03	0.05	0.07	0.09

Once the optimum conditions were decided for the leaching experiments, the PLS from the optimum condition experiment was used for Mn recovery through precipitation. For this purpose, the pH of the system was increased to 5.5 using Na_2S (analytical grade) to precipitate iron in the form of $FeOH_2$ (Ghassa *et al*., 2017) as well as Al and Zn. The PLS was then filtered to separate the precipitated iron. The pH of the filtrate increased again to 8.5 to precipitate out the manganese. The precipitates were analyzed by XRD to characterize the final products. The metal content was also analyzed to calculate extraction recovery efficiency.

Optimization Model

Response Surface Methodology (RSM) based on the Central Composite Design (CCD) was utilized to study and optimize the effects of different factors on Mn recovery using Design-Expert software (Demo v.7.0, Stat-Ease Inc.). RSM is a rigorous mathematical tool for modeling and evaluating problems where the response is influenced by many factors and the main motivation is to get an optimum response (Khosravi *et al*., 2017). CCD was conducted by five factors using 42 tests and 8 replicates at the center points. The α was selected at 2. The ranges and the levels of the factors investigated in the model are given in Table 2.

Results

Leaching and Precipitation

Leaching efficiency of Mn as a function of time was investigated for various parameters, i.e., acid concentration, temperature, solid/liquid ratio and stirring rate. Results for the effect of various parameters on the recovery of Mn from the slag

sample are given in Fig. 2. Although the solid/liquid ratio was found to have a positive effect on the recovery of Mn from slag, the temperature shows a varying impact on the recovery.
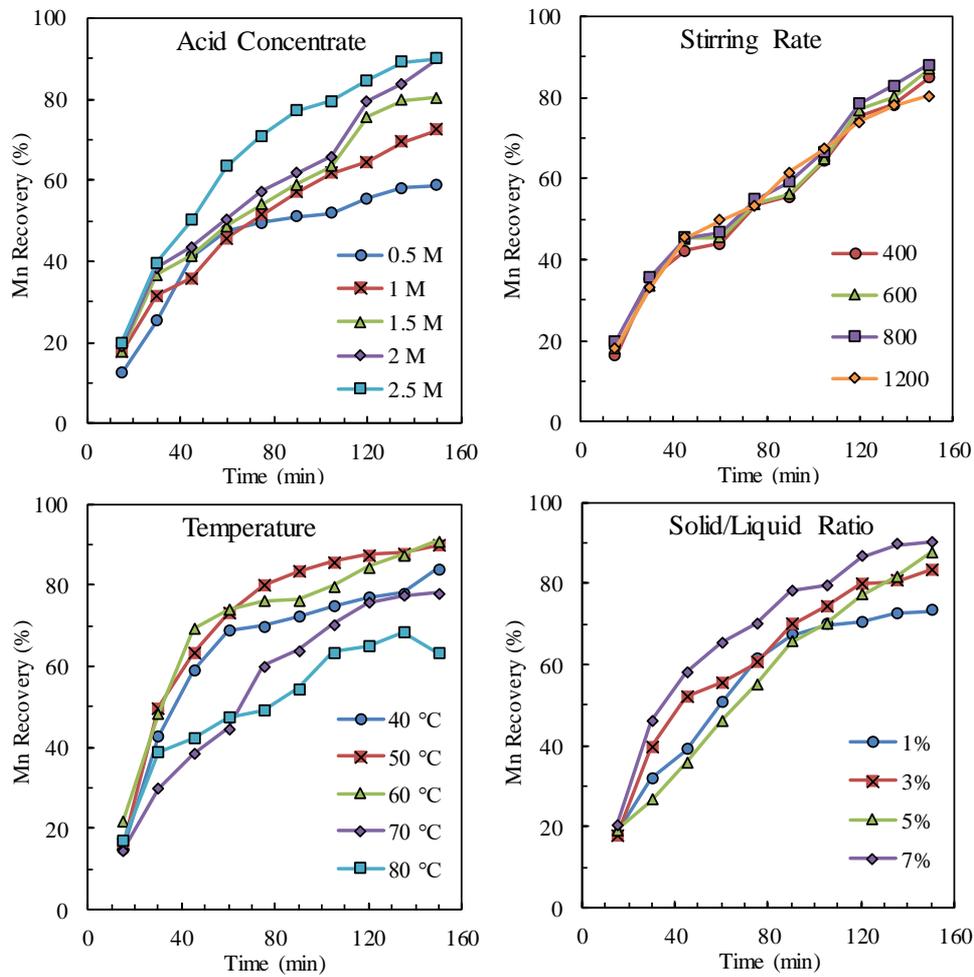
Fig. 2: Effect of various parameters on the recovery of Mn from slag as a function of time
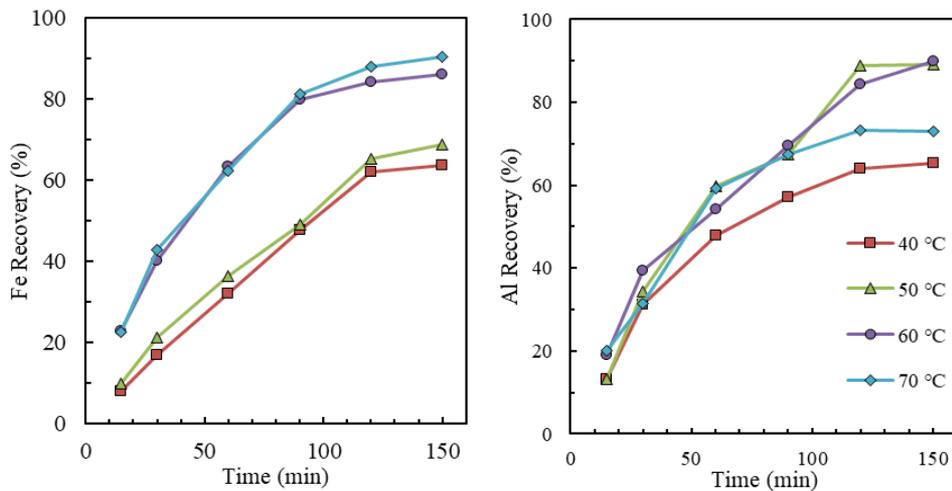
Fig. 3: Effect of temperature on the recovery of Fe (left) and Al (right) from slag as a function of time

751

It was found that the Mn recovery increases by increasing temperature from 40°C up to 60°C. Figure 3 shows the recovery of two other major elements (i.e., Fe and Al) from the slag as a function of temperature. It can be seen from the figure that recovery of both Al and Fe increases rapidly at 60°C, while that of Fe is significantly higher. Although the recovery of Al seems to slightly decrease by a further increase in the temperature, the recovery of Fe remains unchanged after this point. This finding coincides well with previous reports (Liu *et al*., 2009; Yang *et al*., 2015). Considering the amount of Al_2O_3 and Fe_2O_3 and significant recovery of the two elements, it can be concluded that the higher recovery of these reactions hurts the recovery of Mn after 60°C.

After acid leaching, precipitation experiments were conducted at different pH values to selectively recover the Mn from the PLS. After each pH adjustment, the precipitates were filtered and the filtrate solution was analyzed by AAS for the metal content to determine the recovery of the metals. Figure 4 shows the Mn, Zn, Fe, Al and Pb precipitation yields as a function of solution pH adjusted with Na_2S. It was observed that the target elements start to form precipitates in less than 5 min during the precipitation experiments. As it is expected, the precipitation rate increased with increasing pH. The manganese was precipitated at pH 8.5, while Zn, Fe, Al were all precipitated at lower pH values of 2 to 6. Lead, however, mainly remained in the solution even after Mn precipitation at pH 8-8.5. This pattern agrees with the previously reported works for the selective separation of Zn from Mn at pH 2 (Fattahi *et al*., 2016). Therefore, it would be wise to purify manganese sulfate solutions by selectively precipitating the other metals as metal-sulfides at lower pH values (Bryson and Bijsterveld, 1991).

Table 3: Proposed empirical model and ANOVA results for Manganese recoveries

Source	Sum of squares	df	Mean square	f-value	p-value	
Model	15905.97	7	2272.28	40.44	<0.0001	Significant
A	10764.3	1	10764.3	191.58	<0.0001	-
B	694.06	1	694.06	12.35	0.0011	-
C	1170.08	1	1170.08	20.82	<0.0001	-
D	935.48	1	935.48	16.65	0.0002	-
E	392.63	1	392.63	6.99	0.0115	-
AC	1158.01	1	1158.01	20.61	<0.0001	-
C^2	791.42	1	791.42	14.08	0.0005	-
Residual	2359.82	42	56.19	-	-	-
Lack of fit	1688.71	35	48.25	0.50	0.9150	Not significant
Pure error	671.19	7	95.88	-	-	-
Core total	18265.87	49	-	-	-	-
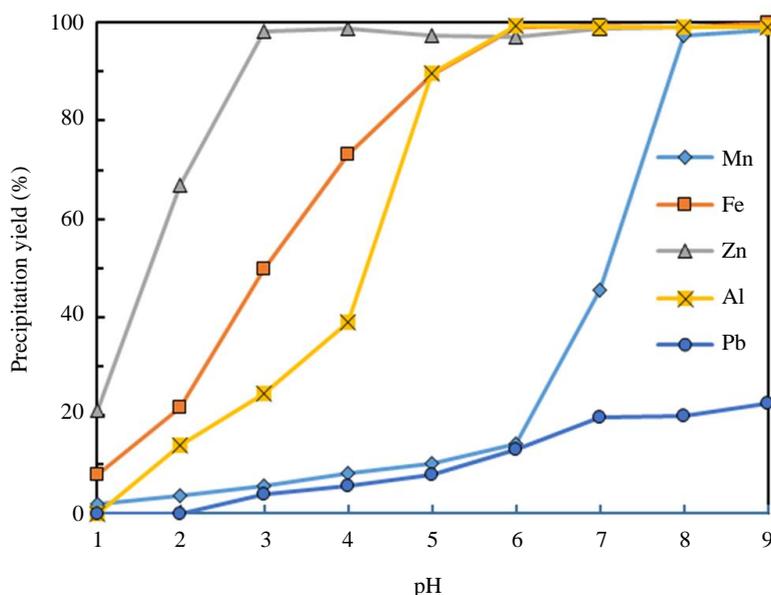
Fig. 4: Precipitation of Mn, Fe, Al, Zn, Al and Pb with Na_2S at different pH solutions

Leaching Optimization

All experiments were designed and analyzed using the Design Expert 7 Trial version (State Ease, Inc., Minneapolis, MN, USA). Central composite experimental design and response data (metals recoveries) are presented in Table 3. Different mathematical models have been fitted to metal recoveries to find the best model. According to Table 3, the mathematical model has a P-value lower than 0.0001, which confirms that models are significant.

As a function of acid concentration (A), stirring intensity (B), temperature (C) and leaching period (D), the final equation describing manganese Recovery (R) in terms of coded factors were obtained:

$$R = -291.56 + 104.97(A) + 0.02(B) + 7.23(C)$$
$$+ 9.67(D) + 156.65(E) - 1.2(A)(C) - 0.05(C)^2$$

The ANOVA confirmed that the equation accurately represented the true relationship between the manganese recovery ratio and the significant variables. The value of 40.44 F indicates the model was substantial. The small *F* and large *P* (P>0.05) fit shortage values mean that the model is appropriate to predict the manganese recovery rate.

Effects of surface plots of variables and 3D response in Fig. 5 display the perturbation plots of the impact of the key factors on the manganese leaching intensity, simulated in Table 3. At a given point in the design space, these plots help to compare the influence of all the variables. A steep slope or curvature of a factor means that the performance of leaching is sensitive to that factor. Figure 5a-5f) specifies the 3D response surface graphs for the relationship between two factors and when the other two factors were held at their center levels of the manganese leaching rate.

Figure 5b, c and d illustrate that manganese leaching recovery increases meaningfully and linearly with increasing the solution acid concentration, solid to liquid and leaching time. It is also noted that in the original phases, the leaching rate rises quickly with an increase in contact moment and then gradually decreases (Figs. 5c and 5d). It's also observed from Fig. 5 That acid concentration is the most important variable and plays a significant part in the leaching method (Figs. 5b, d and e).

Increasing the dose of sulfuric acid increased their leaching rate. The quadratic impact of stirring speed was statistically important, but in practice, it did not have important impacts on manganese leaching (Figs. 5b and 5f). As observed, the decrease in the manganese dissolution occurs at low and high levels of temperature (Figs. 5a, e and f). While the rise in acid concentration value leads to a slight rise in manganese leaching at all concentrations of stirring speed and solid to fluid, it did not have a significant rise. As the acid concentration was increased from 0.5 to 2.5 mol/L, the leaching amount of manganese dissolution increased.

By using design-expert software, the dissolution recovery efficiency of manganese from the slag solution was optimized to achieve maximum dissolution recovery. Figure 6 indicates the trend towards the optimum point in the motion factor. Moving the parameters into the optimum point decreased the recovery of manganese, as shown. The optimum process parameters were two molars for acid concentration, 2.5 h for leaching time, 1000 rpm for stirring speed and 0.07 g/L for solid to liquid. Under these circumstances, the manganese dissolution effectiveness was approximately 91%. It can be discovered in Fig. 6 that the ranking of important variables is as follows: A > D > C > B. Besides, 3D response surface plots were used to obtain a clearer knowledge of the impact of variables on manganese regeneration as shown in Fig. 6. These plots provided data on the main effect of four variables. Figure 7 presents the correlation between acid leaching experimental data and the model data. The correlation coefficient (0.87) shows that the experimental test validates the proposed model.

Leaching Thermodynamics

According to XRD analysis, the manganese orthosilicate mineral, tephroite (Mn_2SiO_4) is the main mineral containing Mn in the ZPS. To the best of our knowledge, this mineral is not reported as the containing Mn mineral in ZPS; hence no literature was found in terms of its extraction as a secondary source. The chemical reaction for the dissolution of tephroite in an acidic medium is given in Equation 3:

$$Mn_2SiO_4 + 4H^+ \rightarrow 2Mn^{2+} + H_4SiO_4$$
$$\Delta G_r^0 = 156.47 \frac{kJ}{mol} \tag{3}$$
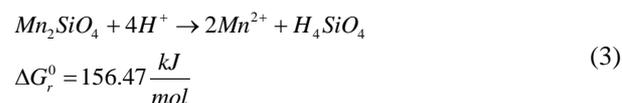
The equilibrium is constant for Equation 3 can be redefined as Equation 4, which combined with Equation 5 will lead to Equation 6:

$$k = \left[Mn^{2+} \right]^2 / \left[H^+ \right]^4 \tag{4}$$

$$pH = -\log \left[H^+ \right] \tag{5}$$

$$\log k = 2\log \left[Mn^{2+} \right] + 4pH \tag{6}$$

Thus, the ion concentration of Mn^{2+} can be calculated from Equation 7:

$$\left[Mn^{2+} \right] = 10^{\left(\frac{1}{2}\log k - 2pH \right)} \tag{7}$$

where, log*k* can be calculated from the equation ΔG_r° =-2.303RT log*k*. The dissolution of manganese depends on the equilibrium constant and pH based on

Equation 5. Manganese in tephroite exists as Mn^{2+} ($2MnO.SiO_2$), unlike another commercial mineral (e.g., pyrolusite), which contains insoluble MnO_2. Acid leaching is carried out directly for minerals containing MnO, while treatment by reduction roasting followed by acid leaching (Feng *et al*., 2013; Yang *et al*., 2013; Zhang *et al*., 2013; Zhao *et al*., 2010) or direct reductive leaching with various reducing agents such as hydrogen peroxide (El Hazek *et al*., 2006; Nayl *et al*., 2011) oxalic acid (Sahoo *et al*., 2001) and sulfur dioxide (Sun *et al*., 2013) is employed for obtaining manganese from MnO_2.
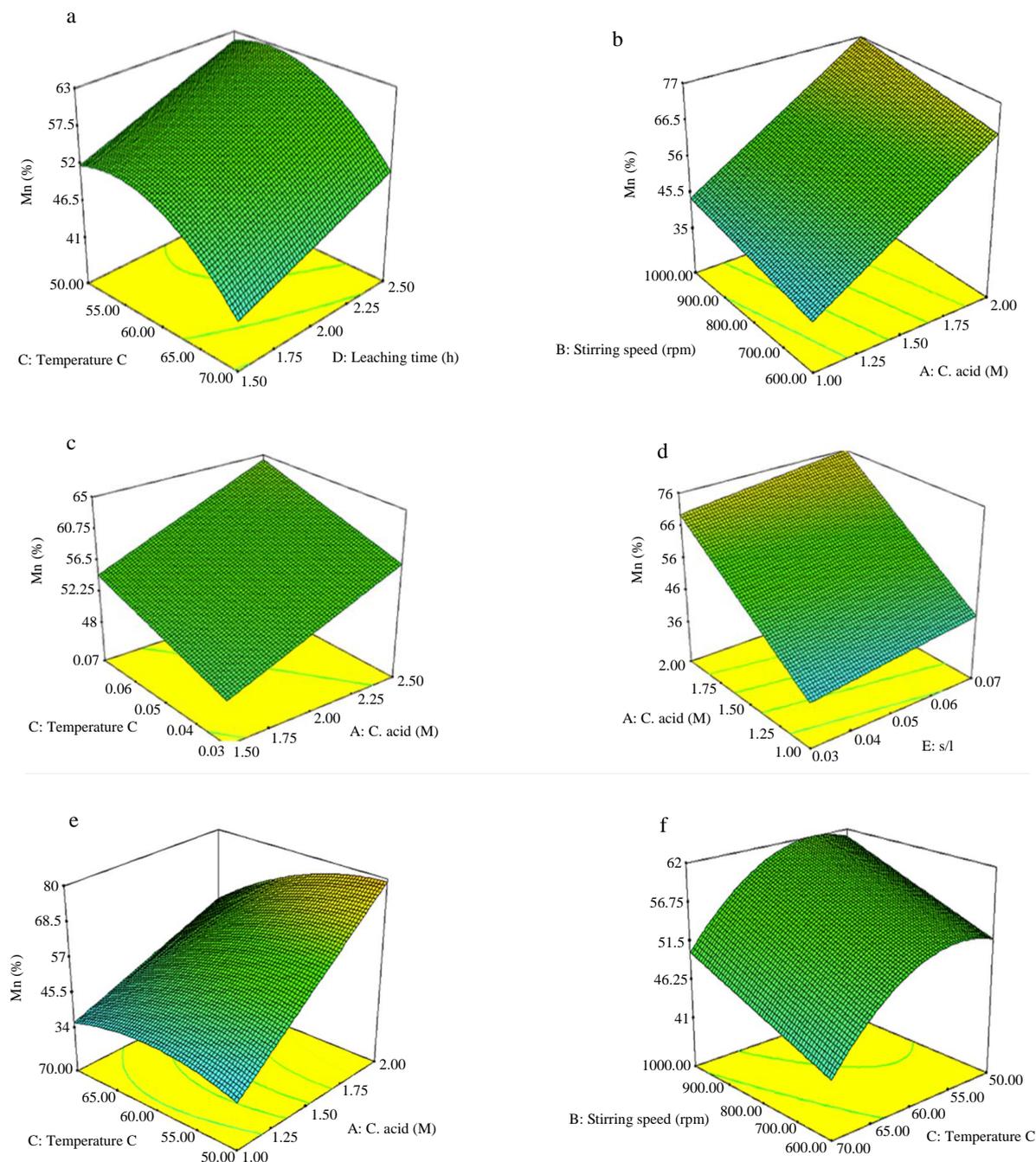
Fig. 5: 3D surface response plots showing the impact of two variables on manganese recovery percentage: (a) Temperature and leaching time; (b) stirring speed and acid concentration; (c) solid to liquid and leaching time; (d) acid concentration and solid to liquid; (e) temperature and acid concentration; (f) stirring speed and temperature
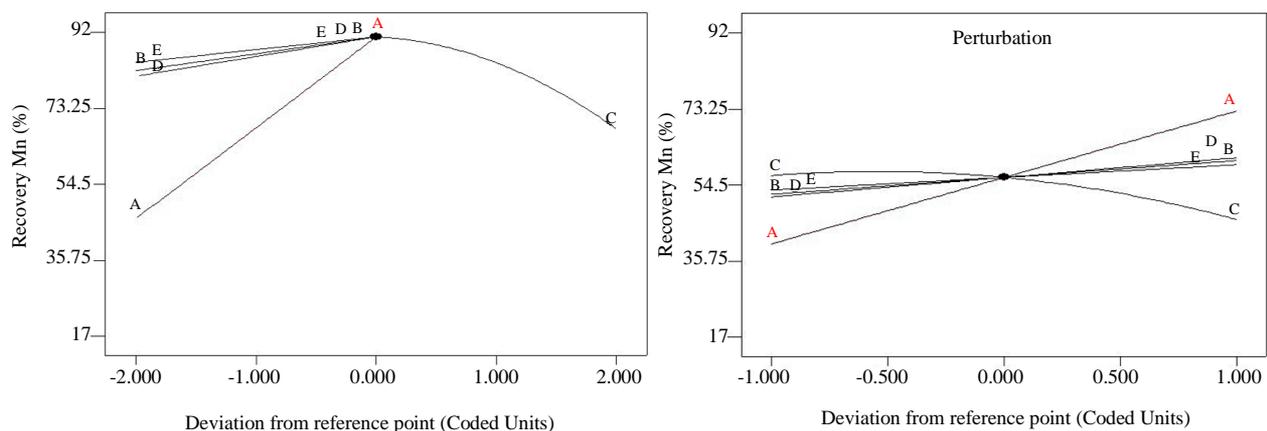
Fig. 6: Left: Perturbation plot showing the relative significance of factors on Mn recovery percentage, right: Perturbation plot showing the optimal conditions of factors to obtain the maximum recovery percentage of manganese
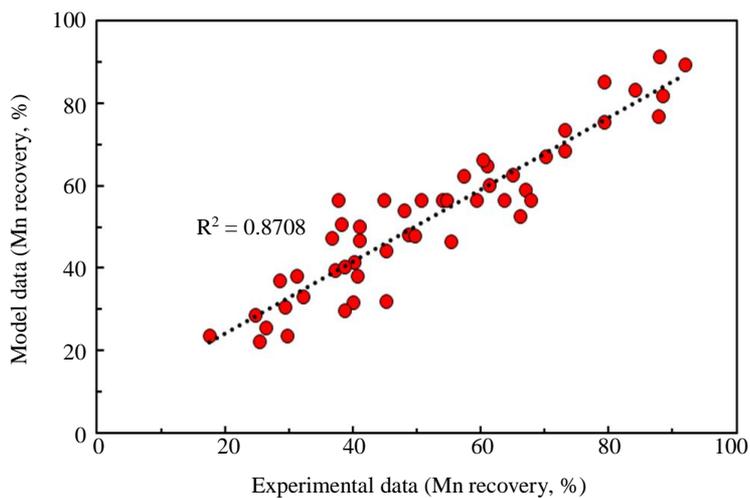
Fig. 7: Model versus experimental data correlation for Mn leaching
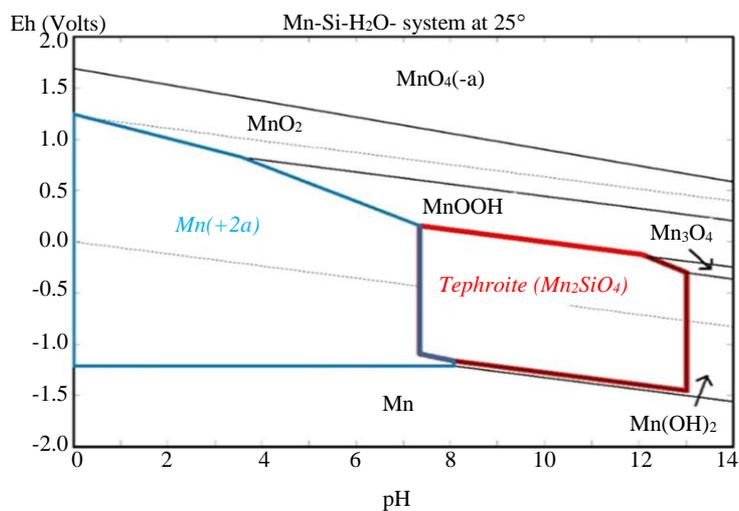
Fig. 8: Eh-pH diagram of the Mn-Si-H_2O thermodynamic system at 25°C drawn by HSC 6.0 chemistry software. The concentration of Mn and Si is equal to 0.1 molars

The Eh-pH diagram is established for the Mn-Si-H$_2$O system at 25°C to provide a better understanding of mineral dissolution and oxide formations boundaries using HSC 6.0 chemistry software (Outokumpu Research, Finland). The dotted lines in Fig. 8 represent the stability region of H$_2$O. As can be seen from Fig. 8, Mn is stable in the wide range of pH and potential in the forms of MnO$_2$, MnOOH, Mn$_3$O$_4$, Mn$_2$SiO$_4$, Mn(OH)$_2$ and Mn. The dissolution of tephroite has been controlled by both potential and pH. When pH falls from neutral to acid region in almost a wide window of Eh, Mn^{2+} is stable, denoting the dissolution of the mineral. Hydrogen ions contributed to metal dissolution (Equation 3 and Fig. 8). The system of Mn-Si-S-H$_2$O was drawn by the same software as well as Spana software (Royal Institute of Technology, Sweden), but no other species were found to coordinate to the metal. When in acidic media, the Eh of the system is too high (more than 1.2 V) or too low (less than -1.2 V), Mn^{2+} will convert to more stable species of MnO$_2$ and Mn, respectively.

Discussion

The recovery of Mn increases by increasing acid concentration as a function of time. On the other hand, it was found that the recovery of Mn is not significantly affected by the stirring rate. This indicates that the convection through the system has a minor effect on the Mn leaching. After 60°C, the recovery of Mn decreased by increasing temperature up to 80°C. One possible reason for this discrepancy can be the presence of other compounds in the slag, which may start to consume the acid at higher temperatures. The proposed mathematical models for the prediction of metal recoveries were shown in Table 3. The results indicated that data should transform to square root format for zinc and lead recoveries to achieve the most significant model; while mathematical models for other metals did not need any transformation-data gathered from different mathematical models (Linear, 2FI, quadratic and cubic) as well as Variance Analysis (ANOVA) showed that manganese dissolution was best described with a quadratic model. In addition, by adding the dose of sulfuric acid the leaching rate increases.

Beside aforementioned, although the Mn surface stays in the divalent oxidation state over a wide range of natural water conditions, higher oxidation states may be reached by the metal and the net surface chemistry can be influenced by such oxidation.

Finally, when in acidic media, the Eh of the system is too high (more than 1.2 V) or too low (less than -1.2 V), Mn^{2+} will convert to more stable species of MnO$_2$ and Mn, respectively.

Conclusion

A hydrometallurgical route to manganese silicate from spent zinc plant residue has been proposed in this investigation. The results have shown the route is technically viable to treat this kind of residue. Manganese can be extracted from ZPS ore in sulfuric acid medium.

Also, the results of leaching tests showed that manganese is effectively recovered and reached a maximum of 91.95%. To determine, model and optimize the influential variables, a response surface method using a central composite design was implemented. The optimum conditions for this leaching are an H$_2$SO$_4$ concentration of 2 mol/L and a solid/liquid ratio of 0.07 g/mL at 50°C for 150 min and an Agitation speed of 1000 rpm. Under these conditions, a manganese leaching efficiency greater than 91.16% is achieved, with a corresponding extraction of iron 22%, lead 23%, zinc 68% and aluminum 64%.

In addition, a quadratic model was developed to explain the behavior of the manganese mechanism of recovery. By Analysis Of Variance (ANOVA), the importance of independent variables was evaluated.

Besides, according to XRD analysis, the manganese orthosilicate mineral, tephroite (Mn$_2$SiO$_4$) is the main mineral containing Mn in the ZPS.

Furthermore, when pH falls from neutral to an acid region in almost a wide window of Eh, Mn^{2+} is stable, denoting the dissolution of the mineral. Hydrogen ions contributed to metal dissolution.

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Author's Contributions

Rasoul Khosravi: Is the idea owner, did the primary lab tests and data analysis.

Rasoul Fatahi: Did lab works and financial support.

Hossein Siavoshi: Did idea development, design the figures and writing manuscript.

Fatemeh Molaei: Was in charge of overall direction, planning and manuscript writing.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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