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RECOVERY OF VALUABLE METALS FROM ZINC PLANT RESIDUE THROUGH SEPARATION BETWEEN MANGANESE AND COBALT WITH N-N REAGENT

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Abstract: Recovery and separation of cobalt and manganese from one of zinc plant residues (ZPR), namely hot filter cake (HFC) using a hydrometallurgical process was studied. The process is carried out in four steps as follows: (1) washing zinc, (2) reductive leaching with hydrogen peroxide, (3) cadmium cementation with zinc powder and (4) separation of cobalt from manganese with beta naphthol. In this research, the separation between manganese and cobalt from the HFC using N-N reagent was investigated. The influence of several parameters on the course of the reaction such as N-N quantity, pH, temperature and reaction time was also examined. The optimum separation conditions were found to be N-N quantity: 8 times of stoichiometric value, time: 30 min, temperature: 25 °C and pH = 1.5. Using the optimized conditions, the cobalt and manganese precipitation was nearly 99% and 0%, respectively. A kinetic study of manganese precipitation through N-N reagent has been carried out to assess the effect of kinetics parameters. The data obtained for the leaching kinetics indicated that the precipitation of manganese is an ash diffusion controlled reaction and the reaction activation energy is equal to 1.4kJ/mol.

Keywords: *zinc plant residue, manganese, cobalt, beta naphthol, kinetics*

Introduction

The production of non-ferrous metals from primary and secondary material results in the generation of a wide variety of wastes and residues. They are a result of metals separation that is necessary for the production of pure metals from complex sources. These wastes and residues result from different stages of processing as well as from the flotation, slags, slimes and flue dusts systems (Florijn et al., 1993, Hatch, 2000, Ross, 1994, Wentz, 1989). These wastes are activated through certain processes such

as grinding, leaching, roasting, smelting, quenching, etc. Exposure of these wastes to atmospheric oxygen and moisture results in solubilization of toxic metals which may dramatically affect the water quality and biological life in surface waters. The potential release of toxic heavy metals from such by-products and waste materials to the surface and ground water is of particular concern (Altundogan et al., 1992, Tumen, 1988, Tumen et al., 1991; 1992).

The hydrometallurgical processes are environmentally and economically more suitable to treat even low zinc containing materials on small scale. They can process secondaries containing different impurities. Zinc oxide ores are usually concentrated through flotation or gravity, where the metal recovery is low and the operating cost is high (Jha et al., 2001, Safarzadeh et al., 2005). Different studies have been carried out throughout the world to recover valuable metals from zinc plant residues (ZPR). For example, Kul and Topkaya (2008) studied the recovery of germanium and other valuable metals from ZPR of Cinkur Zinc Plant. In another study, Wang and Zhou (2002) recommended a hydrometallurgical process for the production of cobalt oxide after inspecting the recovery of cobalt from ZPR. Raghavan et al. (2000) described hydrometallurgical processing of lead-bearing materials generated at zinc plants. In their approach, lead sulfate residue was treated with brine solution and then lead was cemented-out from resultant filtrate using aluminum scrap. With initial lead ion concentration of 4.5 g/dm^3 , 97.1% of lead was extracted. Abdollahi et al. (2006) extracted zinc and lead from Iranian zinc plant residues using brine-leaching method. They blended the residue with H_2SO_4 at 70°C and then for lead recovery, after zinc extraction, the residual solid was subjected to brine leaching with NaCl . Lead content of brine-leaching filtrate was cemented by metallic aluminum. Cementation efficiency for lead content of 16.36 g/dm^3 was about 97–98%. The brine leaching of lead-bearing ZPR of NILZ plant was reported (Farahmand et al., 2009). Safarzadeh et al. (2009) studied the recovery of Zn, Ni and Cd from Ni-Cd residue. Under the optimum collective leaching conditions, t : 150 min, T : 45°C , stirring speed: 500 rpm, S/L : 1/13 and $\text{pH} = 1.3\text{--}1.5$, the maximum metal recoveries were 99.95%, 98.30% and 97.50% for Zn, Cd and Ni, respectively. Also cementation efficiencies for cadmium and nickel were 98.95% and 99.98%, respectively.

Eivazi et al. (2008) reported the best condition for extraction of zinc, cobalt and manganese from ZPR of NILZ plant. Their process included: washing at optimum conditions: $\text{pH} = 3$, $S: L$ ratio of 1:4, 40°C , 90 min; Reductive leaching with: 20 g/dm^3 sulfuric acid, $S: L$ of 1:10, 3%(V/V) hydrogen peroxide and ambient temperature; separation of zinc, manganese and cobalt by solvent extraction using 20%D2EHPA+5%TBP in kerosene, 25°C and $O: A$ ratio of 1:1. Zinc was separated from manganese and cobalt at $\text{pH} = 1.5$. Then, manganese was purified from cobalt at $\text{pH} = 2.9$.

In the zinc plant located in Zanjan, Iran, a leach-electrolysis process is practiced for zinc production. In this process, number of filter cakes is generated daily as by-products. These wastes are stored for valuable elements' recovery in the future and

dumped in open stockpiles where they may lead to heavy metal pollution problems. In these plants three types of wastes are produced: leaching filter cake, Co purification filter cake (or Hot Filter Cake) and Ni-Cd purification filter cake. All of the filter cakes have high levels of heavy metals (Sedaghat et al., 2008).

In this study the possibility of separation of manganese and cobalt with N-N reagent from zinc plant residues (Co filter cake) has been studied. The first step in the metals recovery experiments was the low sulfuric acid washing of Co filter cake samples. After obtaining the pregnant wash solution with the optimum washing recoveries, the solution was leached with hydrogen peroxide in order to recover cobalt and manganese. Subsequently, cadmium was removed from pregnant solution with zinc powder. Finally, manganese and cobalt were separated with N-N reagent. Hence, the objectives of this study was to investigate the role of main factors such as N-N quantity, temperature, pH and reaction time, and also to determine what process controlled the rate of the dissolution of Mn or what kinetic model could be applied. At last, a conceptual flowchart diagram of the process for extraction of valuable metals from zinc plant residue was proposed.

Experimental

Materials and methods

Cobalt filter cake for the leaching study was obtained from Sane Rooy Co., Zanjan, Iran. After drying, the filter cake was ground and homogenized. The chemical analysis was carried out with a Perkin-Elmer AA300 model atomic absorption spectrophotometer. The chemical analysis of the filter cake is given in Table 1. As can be seen from Table 1, the filter cake is mostly composed of zinc and manganese.

Table 1. Chemical analysis of the Co purification filtercake

Content [wt.%]					
Co	Mn	Zn	Ni	Cd	Ca
1.19	9.1	14.66	0.07	0.35	6.64

Separation between manganese and cobalt was examined encompassing four parameters of pH, temperature, N-N quantity and contact time using beta naphthol. For each parameter six levels were chosen as shown in table 2.

Table 2. Special parameters in separation of manganese and cobalt

Parameters	Units	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
pH	–	1.5	2	2.5	3	3.5	4
Temperature	°C	25	40	50	60	70	80
N-N quantity	-	6	7	8	9	10	11
Time	Min	15	30	45	60	75	90

Procedure and equipment

Experiments were carried out in a glass beaker of 1 dm³ volume equipped with a mechanical stirrer submerged in a thermostatic bath. Mechanical stirrer (Heidolf RZR 2020) had a controller unit and the bath temperature was controlled using digital controller (within ± 0.5 °C). For minimizing aqueous loss when the system is heated, a reflux condenser mounted on top of the cell. After adding 1 liter of solution to the reaction vessel and setting the temperature at the desired value, a specific weight of additives were added to the reactor while stirring the content of the reactor at a certain speed. At the end of the reaction period, the contents of the beaker were filtered and the amounts of manganese and cobalt in the filtrate were analyzed.

Results and discussion

Washing of zinc

Based on the results from washing experiments in the previous study (Eivazi et al., 2008) for zinc removal, the following optimum washing conditions were chosen: H₂SO₄ concentration 200 g/dm³, 25 °C, the liquid to solid ratio (L/S) 8:1, pH = 1 and reaction time: 120 min. Using the optimized conditions, the zinc recovery was nearly 96%. After completion of the washing experiment, the washing residue was filtered, washed, dried and weighed. The analytic result of the washed filter cake is given in Table 3.

Table 3. Chemical analysis of the washed filter cake

Content [wt.%]					
Co	Mn	Zn	Ni	Cd	Ca
1.31	11.13	1.77	0.04	0.27	12.36

Reductive leaching with hydrogen peroxide

After sulfuric acid leaching in washing stage, the obtained filter cake was subjected to reductive leaching to investigate the recovery of cobalt and manganese. Cobalt and manganese dissolution is easily performed from ZPR using dilute sulfuric acid solutions containing hydrogen peroxide as a reducing agent. The most suitable conditions were investigated by Eivazi et al. (2009), as follows: sulfuric acid concentration: 30 g/dm³, amount of hydrogen peroxide: 3% (V/V), pulp density: 100 g/dm³, leaching time: 45 min and ambient temperature. Based on the optimum conditions, more than 90% of Co, Mn and Zn could be extracted. The chemical analysis of the achieved filtrate in this stage is shown in Table 4.

Table 4. Chemical analysis of the filtrate

Content [g/dm ³]			
Co	Mn	Zn	Cd
1.18	8.58	1.45	0.035

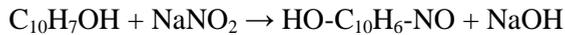
Cadmium cementation with zinc powder

Based on the results from cadmium cementation experiments in the previous study for cadmium removal, the following optimum conditions were chosen: pH = 3.5, Temperature: 25 °C, stirring speed: 100 rpm, zinc powder: 10 time of stoichiometric quantity of cadmium and reaction time: 30 min. Based on the optimized conditions, nearly 97% of cadmium was removed.

Separation between manganese and cobalt using N-N reagent

Preparation of N-N reagent

To make N-N reagent, three materials such as beta naphthol, sodium nitrite and sodium hydroxide were used. The nitrosation reaction of beta naphthol is generally shown as follows:



The ratio of beta naphthol, sodium nitrite and sodium hydroxide in weight has been decided as follows: beta naphthol: 144 g, NaNO₂: 69 g and NaOH: 40 g. Since beta naphthol is hardly soluble in cold water, beta naphthol, sodium nitrite and sodium hydroxide were mixed with cold water and heated to 70 °C through agitation for two hours.

Investigation of effective parameters

Effect of pH

Experiments were carried out to investigate the effect of pH on the separation of manganese and cobalt. As can be seen in Fig. 1, maximum separation between manganese and cobalt is in pH of 1.5. In this pH, recovery of manganese and cobalt was 94.56% and 0% respectively. Therefore, to investigate the other separation parameters, the pH = 1.5 was chosen for the optimum pH.

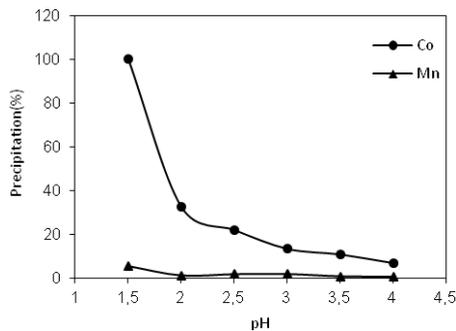


Fig. 1. Effect of pH on the separation of manganese and cobalt for various pH (N-N quantity: 8 times of stoichiometric value; temperature: 25 °C; time: 15 min; stirrer speed: 900 rpm)

Effect of N-N quantity

The effect of N-N quantity on the separation between manganese and cobalt was investigated in the range of 6 to 11 times of stoichiometric value. The results are presented in Fig. 2. As it can be seen in Fig. 2, separation of manganese and cobalt increases with N-N quantity. The maximum manganese and cobalt recovery at N-N quantity equal to 8 times of stoichiometric value after 15 min were 94.56 and 0%, respectively. Therefore, the N-N quantity equal to 8 times of stoichiometric value was chosen for the optimum N-N quantity to investigate the other parameters.

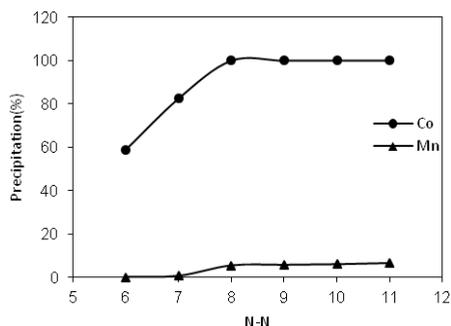


Fig. 2. Effect of N-N quantity on the separation of manganese and cobalt for various N-N amount (pH = 1.5; temperature: 25 °C; time: 15 min; stirrer speed: 900 rpm)

Effect of reaction time

Experiments were carried out to investigate the effect of reaction time on the separation between manganese and cobalt. As it shown in Fig. 3, the optimum precipitation of the cobalt and manganese were 99% and 0%, respectively, at reaction time of 30 min. Therefore, the time: 30 min was chosen as optimum time.

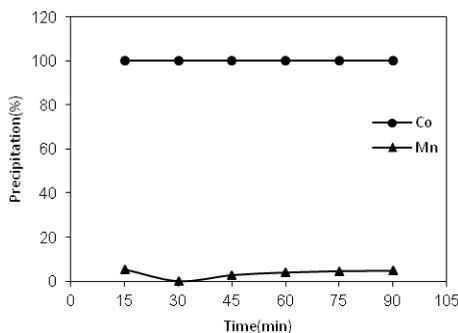


Fig. 3. Effect of reaction time on the separation of manganese and cobalt for various times (N-N quantity: 8 times of stoichiometric value; temperature: 25 °C; stirrer speed: 900 rpm; pH = 1.5)

Effect of temperature

Figure 4 shows the effect of temperature on the separation between manganese and cobalt. As it shown in Fig. 4, increasing the temperature up to 40 °C resulted in a decrease in manganese recovery. The maximum recovery of Mn was noticed in the temperature of 25 °C that was equal to 99%.

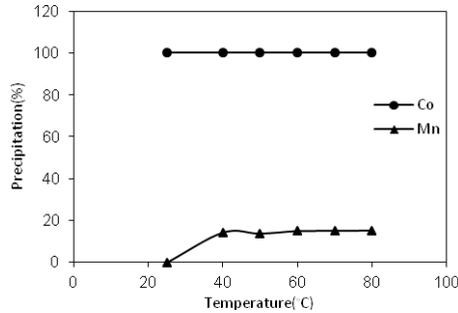


Fig. 4. Effect of temperature on the separation of manganese and cobalt for various times (N-N quantity: 8 times of stoichiometric value; time: 30 min; stirrer speed: 900 rpm; pH = 1.5)

Kinetics of separation between manganese and cobalt

The shrinking core model (SCM) was used to describe the leaching reaction. Therefore, three different models can be considered as reaction mechanism with their constant rate equations which will be discussed in the following section.

Film diffusion control for spherical particles

The fraction of manganese reacted at any time, t , in a film diffusion control situation can be calculated from the following equation (Levenspiel, 1999):

$$X_{Mn} = kt \quad (1)$$

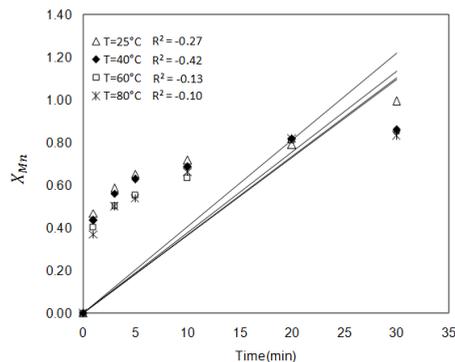


Fig. 5. Plot of X_{Mn} vs. time for different temperatures (N-N quantity: 8 times of stoichiometric value; time: 30 min; stirrer speed: 900 rpm; pH = 1.5)

where X_{Mn} stands for the fraction of manganese reacted and k (min^{-1}) is reaction rate constant. Based on the experimental data shown in Fig. 5, the left-hand side of Eq. (1) is plotted against time. The values of the correlation coefficient R^2 for linearity of the plot are very far from the normal state. At all of the temperatures, the experimental data deviates further from a linear form. None of the straight lines can be considered close enough to fit the experimental data to suggest a film diffusion model for the process.

Ash diffusion control for spherical particles

Diffusion of Mn^{2+} through the blanket of ash at any time, t , can be calculated from the following equation (Levenspiel, 1999):

$$1 - 3(1 - X_{Mn})^{2/3} + 2(1 - X_{Mn}) = kt. \quad (2)$$

In order to test the possibility of diffusion through the ash, the left hand side of Eq. (2) was plotted against time (Fig. 6). It is obvious that the data are well fitted to the corresponding lines. Therefore, the diffusion through the ash could be rate determining step in the process.

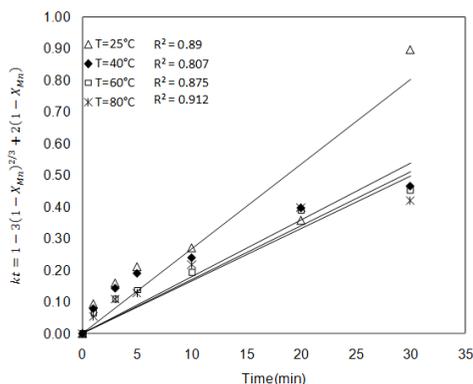


Fig. 6. Plot of $1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)$ vs. time for different temperatures (N-N quantity: 8 times of stoichiometric value; time: 30 min; stirrer speed: 900 rpm; pH = 1.5)

Chemical reaction control for spherical particles

The fraction of manganese reacted at any time, t , in a chemical reaction control process can be calculated from the following equation (Levenspiel, 1999):

$$1 - (1 - X_{Mn})^{1/3} = kt. \quad (3)$$

The left-hand side of Eq. (3) is plotted against reaction time in Fig. 7. By comparing Figs. 5–7, it is indicated that the R^2 values for Fig. 6 are closer to 1 than those of Figs. 5 and 7. Therefore the data can be correlated to an ash diffusion control model and diffusion of Mn^{2+} through the blanket of ash controls the reaction rate.

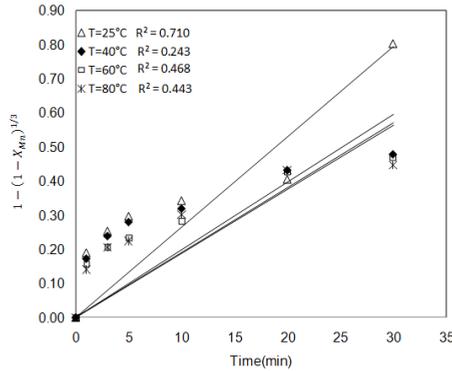


Fig. 7. Plot of $1 - (1 - \alpha)^{1/3}$ vs. time for different temperatures (N-N quantity: 8 times of stoichiometric value; time: 30 min; stirrer speed: 900 rpm; pH = 1.5)

Activation energy

The temperature dependence of the reaction rate constant (k) can be calculated from the Arrhenius equation (Levenspiel, 1999):

$$k = A \exp\left(\frac{-Q}{RT}\right) \tag{4}$$

where A represents the frequency factor; Q (kJ/mol) is the activation energy of the reaction; R is the universal gas constant and T is the absolute temperature. The values of k at different temperatures can be calculated from the slope of the lines shown in Fig. 6. The results obtained from Figs. 5–7 indicate that the dissolution rate of manganese is controlled by the diffusion and not by surface chemical reactions. Generally, a high value of activation energy indicates that the process is “strongly” influenced by temperature and, therefore, the rate-controlling step could be the

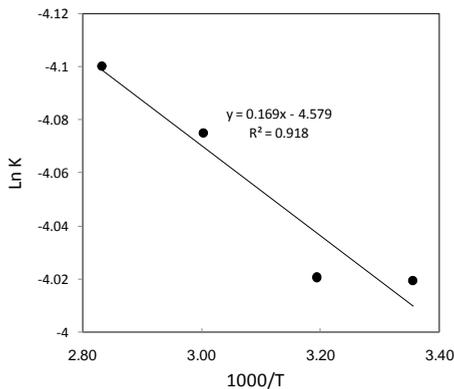


Fig. 8. Arrhenius plot of reaction rate against reciprocal temperature (N-N quantity: 8 times of stoichiometric value; time: 30 min; stirrer speed: 900 rpm; pH = 1.5)

reaction at the solid surface. Conversely, a low value of activation energy indicates that the process is “weakly” influenced by the temperature and the rate-controlling step could be the mass transport of reagents or products through the reaction product. Arrhenius plot considering the apparent rate constants was obtained by applying Eq. 2 to leaching experimental data. As can be seen in Fig. 8, the calculated activation energy was 1.4 kJ/mol which clearly suggests ash diffusion control for the process.

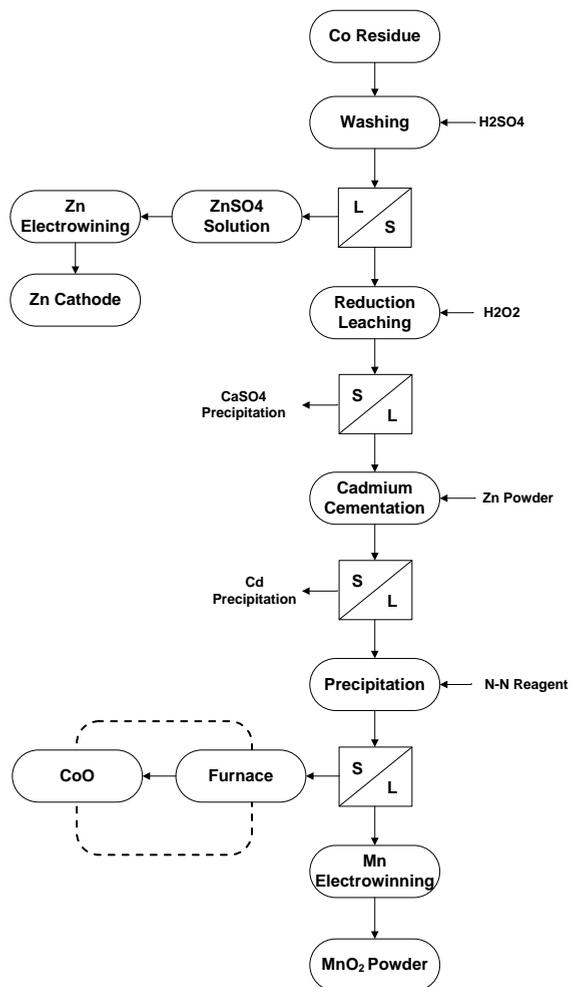


Fig. 9. Flow diagram for the recovery of zinc, manganese and cobalt from zinc plant residues

Working flow sheet

Finally, taking the findings of this study into account, a simplified flow diagram (Fig. 9) was proposed for the process, showing the successive stages based on the process conditions. The laboratory scale experiments including washing by dilute sulfuric

acid, reductive leaching with hydrogen peroxide, cadmium cementation with zinc powder and separation between manganese and cobalt by N-N reagent were performed in order to produce several valuable products from zinc plant residue. Zinc has been recovered from hot filter cake by washing. Filtrate of this stage was sent for electrowining to produce zinc cathode. Residue from previous stage has been leached with hydrogen peroxide for recovering manganese and cobalt. In this stage there was a residue including CaSO_4 . Filtrate has been used for cadmium removal with zinc powder. Residue of this stage contains cadmium with high grade. Filtrate had manganese and cobalt. Separation between above-mentioned elements was carried out with N-N reagent. After filtration, residue contains cobalt along with beta naphthol. Beta naphthol was burned by furnace and then cobalt oxide was achieved. After cobalt removal, manganese can be recovered from solution by electrowining.

Conclusion

In this research, a hydrometallurgical process has been applied for recovery of valuable metals from Hot Filter Cake of zinc production plant. This process has several stages including: (1) washing zinc, (2) reductive leaching with hydrogen peroxide, (3) cadmium cementation with zinc powder and (4) separation between cobalt and manganese with N-N reagent. This study has mainly focused on the separation of manganese and cobalt from ZPR with N-N reagent. The effect of operating conditions such as N-N quantity, time, pH and temperature on separation between manganese and cobalt was studied. As a result, the ultimate optimum leaching conditions were found to be time: 30 min, temperature: 25 °C, stirring speed: 900 rpm, N-N quantity: 8 times of stoichiometric value and pH = 1.5. Under this condition, precipitation of cobalt and manganese were 99% and 0%, respectively. Finally, the final precipitate was burned to remove beta naphthol and then cobalt oxide was achieved. A shrinking core model can be used to describe the dissolution kinetics of ZPR in dilute sulfuric acid solution. The dissolution process was found to be controlled by diffusion through a product layer. The activation energy of the dissolution process was found to be 1.4 kJ/mol in the temperature range of 25–80 °C. The low value of activation energy predicts that Mn extraction should be less sensitive to temperature.

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