TECHNOLOGY BASED ON SODIUM ALKALINE ROASTING AND HYDROMETALLURGICAL METHODS OF MANGANESE EXTRACTION FROM SLAGS OF THE STEELING INDUSTRY

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Abstract

This article analyzes the technology of sodium hydroxide roasting and hydrometallurgical processing for extracting manganese from metallurgical slags. The study tested methods for obtaining a selective solution from slag samples roasted at temperatures of 200°C and 300°C using distilled water and 16% sulfuric acid. Based on EDXRF and XRD analyses, manganese compounds with a purity of up to 34% were isolated, and the ecological and economic advantages of this method were substantiated.

Keywords: manganese, metallurgical slag, sodium hydroxide, hydrometallurgy, sulfuric acid, EDXRF, selective leaching

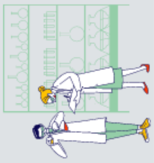
Introduction

Manganese slags are important as a secondary resource in metallurgical waste, and extracting valuable components through their processing is of great importance. In particular, the high content of iron and manganese oxides in the slags formed as a result of steel smelting at the Almalyk Mining and Metallurgical Complex indicates this waste as a promising raw material for processing.

Literature Review

Modern scientific approaches to processing manganese-containing metallurgical slags are mainly based on a combination of hydrometallurgical and pyrometallurgical methods. Highly selective technologies are especially necessary for extracting manganese from slags containing stable orthosilicate phases, such as tephroite (Mn_2SiO_4).

In a study conducted by Ma Y. et al. (2020), the effectiveness of acidic solutions in extracting manganese from the tephroite phase, especially the advantages of sulfuric acid, was



demonstrated. They successfully carried out the transfer of Mn (II) ions into solution using H_2SO_4 under conditions of high temperature and relatively long-term processing [1].

Yang C. et al. (2019), in studies of selective leaching with tephroite-containing slags, ensured the release of manganese without mixing with other metals (for example, Fe, Ca, Al) by controlling the pH level. They experimentally proved that Mn^{2+} can be maximally transferred to solution under low pH conditions (2-3) [2].

Gaskell (2017), in his work on thermodynamic materials science, elaborated on the thermodynamic stability of orthosilicate phase decomposition reactions. According to him, the reaction $Mn_2SiO_4 + 2H_2SO_4 \rightarrow 2MnSO_4 + H_4SiO_4$ is exothermic and is characterized by $\Delta H < 0$ and $\Delta G < 0$, which means the process proceeds spontaneously [3].

Zhang W. et al. (2022) combined experimental and thermodynamic calculations for Mn extraction and showed through graphs how the leaching process changes under the influence of heat. They found that MnSO4 formation becomes even easier with increasing temperature [4].

In the analytical review conducted by Patel R. (2022), important analytical data on the effectiveness and selectivity of precipitation reactions with NaOH and NH4OH during the hydrometallurgical processing of manganese are presented. It has been shown that manganese can be isolated as high-purity compounds by maintaining a pH level of around 8-10 during precipitation [5].

Additionally, Liu X. et al. (2020) in their research proposed energy-efficient and environmentally friendly methods for recovering manganese from metallurgical waste. They emphasize the importance of the initial roasting process in separating manganese and iron from each other [6].

In the regulatory document ASTM Standard D7348-13, it is noted that the presence of reactive components in the material can be assessed by determining the loss on ignition (LOI) of the slag [7].

Research Methodology

Studies were conducted on samples of manganese slag obtained from the Almalyk Mining and Metallurgical Complex. The slag was crushed to -0.1 mm and roasted with sodium hydroxide at 200°C and 300°C. The roasted samples were selectively leached with distilled water, and the resulting solution and sludge were processed separately and neutralized with a 16% H_2SO_4 solution and subsequently with NaOH.

Analysis and Results

The roasting process is a pyrometallurgical process used in the field of metallurgy to alter the composition of metal-containing compounds. It is primarily used in non-ferrous metallurgy to convert copper and zinc sulfides into oxide compounds in special roasting furnaces. The main difference between the roasting process and the smelting process is that during roasting, the temperature is kept below the melting point of the substances.

Due to the high content of iron oxides in the samples brought for processing slag formed during the steel smelting process at the Central Repair and Mechanical Plant of JSC "Almalyk MMC," the sample was roasted with sodium hydroxide to transfer iron oxide into solution, thereby reducing its content in the sludge.

Sodium hydroxide is a substance with strong caustic properties. Considering that this substance melts at a temperature of 300°C, the sample mixed with sodium hydroxide was roasted at 200°C. Since the initial experiments were conducted with samples of -1 mm size and the substances did not fully react in the experimental work, the slag sample was reduced from -1 mm to -0.1 mm for the purpose of roasting with sodium hydroxide.

For roasting, 100 g of a slag sample with a size of -0.1 mm was taken and mixed with 20 g of sodium hydroxide in a special crucible. Roasting was carried out in a muffle furnace at a temperature of 200°C. After the muffle furnace was connected to the power supply and heated to a temperature of 200°C, a special crucible was placed inside, and the start time of the roasting process was recorded. Due to the small amount of slag and sodium hydroxide and the wide surface area of the crucible, the roasting process was carried out for 1 hour. This time was considered sufficient for the sample to react with sodium hydroxide.

The purpose of roasting was to form sodium tetrahydroxoferrate by reacting the iron oxide in the slag sample with sodium hydroxide. This compound has the ability to dissolve in water and reduces the iron content in the main sample during subsequent processes.

$$Fe_2O_3 + 2NaOH \rightarrow 2NaFeO_2 + H_2O \qquad (1)$$

The sample burned for one hour is cooled while remaining inside the furnace. The muffle furnace is disconnected from the power supply and left in this state for one day. The main purpose of leaving it in this state is to satisfy the oxygen demand during cooling, as oxygen is necessary for the reaction between sodium hydroxide and the compounds in the sample.

After cooling for one day, the calcine is selectively dissolved in 200 ml of distilled water. The selective dissolution process was carried out with mechanical stirring for half an hour. The resulting solution was left to settle for another day. After settling for one day, the solution was filtered. The solution and sludge were separated using a vacuum filter. There was no change in the color of the separated solution. When tested with litmus paper, the solution was found to be alkaline, and to neutralize it, a 98% sulfuric acid solution was added until neutralization was achieved. As a result, there were no changes in the solution.

The obtained sludge was treated with diluted sulfuric acid. 200 ml of a 16% sulfuric acid solution was added to the sludge and mechanically stirred for 1 hour. The resulting solution was left to settle for one day. After settling for one day, the solution was filtered, and the sludge was separated. The separated solution was mixed with a 10% sodium hydroxide solution for neutralization. As the solution's pH approached neutral, a blue precipitate formed. To separate the formed precipitate, the solution was first allowed to settle for 6 hours. As a result of settling, the amount of precipitate in the solution increased. The precipitate was separated from the solution using a vacuum filter. To analyze the composition of the separated precipitate, it was dried at 100°C for 1 hour. To study the chemical composition of the obtained precipitate, the samples were analyzed using an Energy Dispersive X-ray Fluorescence (EDXRF) device. The results of the dried precipitate analysis are presented in Table 1, and the X-ray phase analysis in Figure 1.

Table 1 X-ray phase analysis of the precipitate formed during hydrometallurgical processing of slag after primary calcination with sodium hydroxide

Detected items, %									
M	MnO	MgO	Fe_2O_3	SiO_2	CaO	Al_2O_3	Co	K_2O	P_2O_5
%	5,21	0,013	1,12	10,64	3,506	0,553	0,001	0,784	0,00005
M	Se	Br	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,00027	0,00005	0,00754	0,00086	0,00012	0,00013	0,00012	0,00003	0,00019
M	Ti	V	Cr	Ni	Cu	Ga	Ge	As	Oth.
%	0,02659	0,00002	0,0831	0,00718	0,0125	0,00004	0,00002	0,0002	1. 7,7324

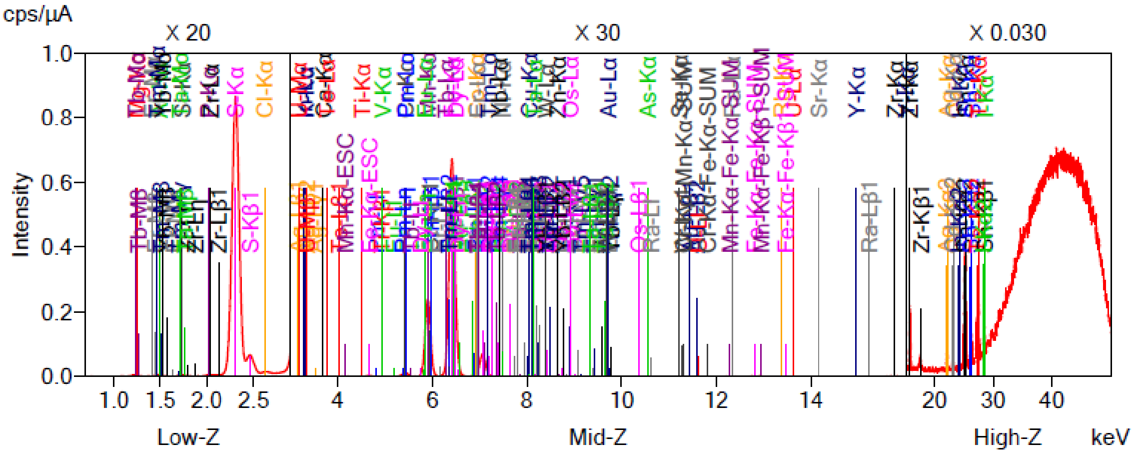


Figure 1. X-ray spectroscopy of the precipitate formed during hydrometallurgical processing of slag after primary calcination with sodium hydroxide.

As can be seen from Table 1, in the experiment conducted at a temperature of 200°C, due to the poor reaction between the sodium hydroxide and the slag sample, the manganese metal content in the resulting precipitate was very low. Therefore, the subsequent experiment was carried out at a temperature of 300°C.

For calcination, 1 kg of a slag sample with a particle size of -0.1 mm was taken and mixed in a special crucible with 200 g of sodium hydroxide. Calcination was carried out in a muffle furnace at a temperature of 300°C. After the muffle furnace was connected to the power supply and heated to a temperature of 300°C, a special crucible was placed inside, and the start time of the calcination process was recorded. Due to the low quantity of slag and sodium hydroxide and the wide surface area of the crucible, the calcination process was carried out for 1 hour. It was determined that this time is sufficient for the sample to react with sodium hydroxide.

After the calcination process was carried out at a temperature of 300°C for 1 hour, it was cooled in the muffle furnace for 2 hours. Cooling time was calculated from the moment the muffle

furnace was disconnected from the power supply. After 2 hours, the calcine was removed from the furnace and left at room temperature for 24 hours. After 24 hours, the calcine was mixed with 200 ml of distilled water for 30 minutes using a special mixer. Then the solution turned dark blue. This indicates the presence of iron and manganese hydroxides in its composition. After stopping the mixing, the solution was left at room temperature for one day to settle. After 1 day at room temperature, the remaining solution was filtered to separate it from the sludge. The X-ray phase analysis of the obtained sludge is presented in Table 2.

Table 2 X-ray phase analysis of the sludge
resulting from selective dissolution of the calcine with distilled water

Detected items, %									
M	MnO	MgO	Fe_2O_3	SiO_2	CaO	Al_2O_3	Co	K_2O	P_2O_5
%	11,91	0,017	2,826	11,66	2,506	0,653	0,001	0,784	0,00007
M	Se	Br	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,00037	0,00006	0,00834	0,00096	0,00022	0,00034	0,00011	0,00002	0,00019
M	Ti	V	Cr	Ni	Cu	Ga	Ge	As	Boshq.
%	0,02659	0,00002	0,0941	0,00718	0,0462	0,00005	0,00003	0,00017	69,1545

The data presented in Table 2 above indicate that the majority of manganese remained in the sludge, while the main portion of iron transferred into the solution. To extract manganese from the obtained sludge, a hydrometallurgical process was implemented.

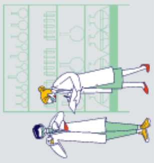
The filtered solution was mixed with 98% sulfuric acid for neutralization. Ammonia solution is added until the solution environment approaches neutral. When the solution medium became neutral, the color of the solution changed to pink. It was determined that manganese in the solution was present in the form of permanganic acid and sodium permanganate. This is because the permanganic acid residue and its salts formed with alkali metals have a pink color.

$$Mn_2O_7 + 2NaOH = 2NaMnO_4 + H_2O \qquad (2)$$

In the aforementioned method, the experimental work continues by first roasting the slag with sodium hydroxide and then selectively dissolving it with acids before hydrometallurgical processing.

The residual sludge from the selective dissolution of the calcine in water was treated with a 16% solution of diluted sulfuric acid. This choice was based on literature indicating that diluted sulfuric acid reacts more effectively than other acids and doesn't require heating during this process. 200 ml of 16% sulfuric acid solution was prepared and mixed with the filtered sludge for 1 hour. The resulting mixture was left to settle at room temperature for 24 hours.

After settling for a day, the solution was passed through a vacuum filter. Filtration yielded a yellowish solution and sludge. Since the filtered solution resulted from sulfuric acid treatment, it was mixed with a 10% sodium hydroxide solution for neutralization. As the solution approached a neutral pH, a blue precipitate formed. To determine the composition of this precipitate, the solution was filtered to separate the precipitate, which was then dried in a muffle furnace at 100°C for 80 minutes. To analyze the chemical composition of the isolated precipitate, samples were examined using Energy Dispersive X-ray Fluorescence (EDXRF)



equipment. The chemical composition of the precipitate is presented in Table 3, while the X-ray phase analysis and X-ray spectroscopy results are shown in Figure 2.

Table 3 X-ray phase analysis of the precipitate obtained from the reaction of the selective leaching solution with sodium hydroxide

Detected items, %									
M	MnO	MgO	Fe_2O_3	SiO_2	CaO	Al_2O_3	Co	Cr_2O_3	P_2O_5
%	43,890	0,4667	1,557	8,940	0,294	4,2878	0,0005	0,9647	27,095
M	Se	Br	Zn	Zr	Nb	Mo	Cd	Pb	Sn
%	0,0012	0,00008	0,0255	0,0016	0,0032	0,356	0,0362	0,00003	0,0384
M	Te	V	Cr	Ni	Cu	Ga	Ge	As	W
%	0,0175	0,0556	0,0325	0,0352	0,002	0,0405	0,0002	0,00018	0,0805

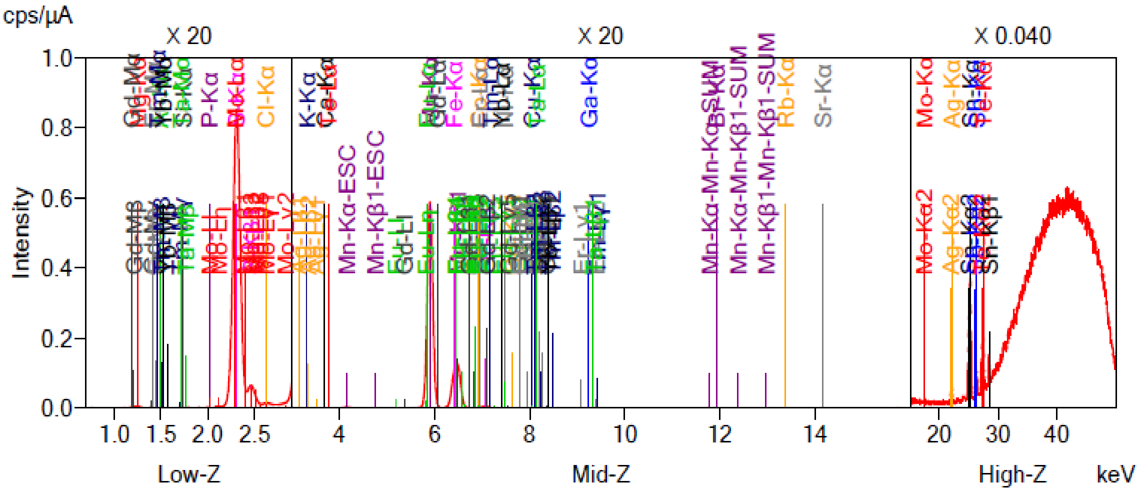


Figure 2. X-ray spectroscopy of the precipitate obtained by the reaction of the resulting solution of leaching with sodium hydroxide

As can be seen from Table 3, the precipitate contains more than 34% manganese, and the iron content is less than 1%.This shows that it is possible to increase the amount of manganese metal extraction by changing certain parameters of the method. Using the above method, the experiment was repeated 5 times, the results obtained were close to the data shown in Table 3 Increasing the temperature during the calcination of slag with sodium hydroxide significantly influenced the release of manganese. At 300°C, the release of Mn was 2 times greater.

Based on the above data, it can be concluded that the extraction of manganese compounds from a slag sample calcined with sodium hydroxide using hydrometallurgical processes is more profitable than methods performed without calcination. However, as a result of the experiment, a certain amount of manganese was observed to pass into the solution. This is due to the fact that as a result of roasting with sodium hydroxide, a certain part of manganese forms a water-soluble compound with sodium hydroxide, and as a result of this, manganese passes into solution as a result of leaching with distilled water.

Conclusion

Experiments have shown the high efficiency of the technology of calcination with sodium hydroxide and hydrometallurgical smelting in the selective extraction of manganese from metallurgical slag. After roasting at 300°C and dissolution with H_2SO_4, up to 34% of pure manganese compounds were isolated using NaOH. This method allows for the recycling of manganese waste in an environmentally and economically beneficial way.

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