Technology for producing high-quality manganese concentrates from ferromanganese concretions and polymetallic manganese-containing ores

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Abstract. The results of studies of ferromanganese concretions enrichment using various solvents are presented. Universal technologies were proposed for processing manganese raw materials, including its autoclave leaching with aqueous solutions of chlorides, which allow manganese to be extracted into solution from compounds of various oxide and carbonate forms. Manganese recovery is over 90%. The introduction of ferrous manganese concretions into the chlorine-calcium enrichment process allows the extraction of manganese to be increased by 2.3, cobalt by 3.2, and nickel by 2.5 times. The leaching of ferromanganese concretions by aqueous solution of hydrochloric acid with the neutralization of its excessive concentration by the introduction of carbonate manganese ore makes it possible to extract non-ferrous metals in the solution of 99.80 – 99.88% and up to 95.4% Mn. As a result of enrichment, manganese, copper-nickel-cobalt and iron concentrates can be obtained.

1. Introduction

Ferromanganese concretions (FMC) are promising sources of raw materials. The most valuable components of FMCs are manganese, cobalt, nickel and copper. Concretions are aggregates of extremely finely fused hydroxides of iron, manganese and clastic-clay material, which occur at the bottom of the Pacific Ocean and the Gulf of Finland. Enrichment of ferromanganese concretions is a necessary stage in its preparation for metallurgical processing.

The analysis of literature data and a physicochemical evaluation of the extraction of manganese and other impurities from manganese-containing raw materials showed that the calcium chloride method is the most promising [1, 2], with which it is possible to obtain a manganese concentrate that meets the highest industry requirements [3,4]. In terms of hardware design, this method is similar to autoclave leaching in alumina production, which has been working smoothly for many years and allows one plant to achieve a productivity of 1 million tonnes or more per year.

A significant part of manganese in ferromanganese concretions is presented in oxide form and only an insignificant part in the form of carbonates, and the calcium chloride process is effective in treating only carbonate manganese ores. An analysis of the literature data, as well as the works of the authors in [3], and preliminary experiments with pure oxide materials, showed that it is most expedient to develop a method for enriching concretions using aqueous solutions of calcium chloride and the addition of solutions of iron chlorides or sulfates, or usage of a salt solution as a solvent acids. In
addition to FMC, polymetallic manganese-containing ores deposits of which are located in Kemerovo Region are of particular interest as raw materials. Along with manganese (up to 54%), these ores contain non-ferrous metal impurities (Ni – 0.5%, Co - 3%, Cu – 0.2%) and a rather high phosphorus content (0.2%).

2. Materials and methods of research

Studies of the chemical enrichment of manganese-containing raw materials were carried out by the method of sampling a solution, precipitation, slag, metal.

The chemical and phase composition of the starting materials and products of their processing was determined by chemical, spectral, and X-ray microanalysis. Extraction of manganese, cobalt, nickel and copper from concretions was evaluated by analyzing the dry solids after leaching and filtrate.

For optimal leaching conditions, we studied the effect of processing time, process temperature, coarseness of concretions crushing, the concentration of calcium chloride in the initial solution, the ratio of iron in the form of sulfates to the consumption of manganese in the charge (kg/kg), as well as the effect of preliminary heat treatment of concretions on the extraction of valuable components.

For this, the concretions of the above composition were crushed to a certain size, mixed with iron sulfate (in the form of FeSO₄·7H₂O) at different ratios between them and autoclaved at temperatures of 180 – 220 °C with an aqueous solution of calcium chloride (600 – 900 g/l). Each experiment was repeated three to four times.

The experiments were carried out in autoclaves with volumes of 75, 100, and 10,000 cm³. During the experiments, exactly the same temperature conditions and pulp mixing were provided. The temperature was automatically adjusted with an accuracy of ± 5 °C.

For the experiments were used:
- concretions - Mnₜₒₒ - 15.17 %; MnO₂ - 21.2 %; Co – .275 %; Ni – 0.46 %; Cu – 0.22 %; Fe₂O₃ – 23.1 %; SiO₂ – 13.74 %; CaO – 2.6 %; MgO – 2.01 %; Al₂O₃ – 3.67 %; P – 0.255 %; moisture – 16.68 %;
- polymetallic manganese ore - Mnₜₒₒ - 48.8 %; Co – 3.0 %; Ni – 0.49 %; Cu – 0.23 %; Feₜₒₒ – 3.1 %; SiO₂ – 17.5 %; CaO – 2.6 %; MgO – 0.68 %; Al₂O₃ – 3.67 %; P – 0.255 %.
- carbonate manganese ore – 26 – 31 % manganese, 8 – 11 % calcium oxide and 1 – 3 % MgO, 2 – 7 % Fe₂O₃, 8 – 17 % SiO₂.
- solutions of iron chloride - FeCl₂ – 220 – 230 g/l, HCl – 60 – 70 g/l, FeCl₃ – 15 – 25 g/l, HSO₄ – 30 – 50 g/l, FeSO₄ – 150 – 200 g/l.

3. Results and discussion

When using calcium chloride as a solvent with the addition of iron sulfate solution, manganese oxide passes into the solution according to the following reaction:

\[ \text{MnO}_2 + \text{MnO} + 2\text{FeSO}_4 + 2\text{CaCl}_2 + 3\text{H}_2\text{O} = 2\text{MnCl}_2 + 2\text{CaSO}_4 + 2\text{Fe(OH)}_3 \]

From the data of table 1 it can be seen that the introduction of iron sulfates into the calcium chloride process can increase the extraction of manganese by 2.3; cobalt – 3.2; nickel – 2.5 times. The results of experiments with concretions of varying degrees of grinding showed that with a decrease in their size, the extraction of manganese, cobalt, nickel and copper increases markedly and when using concretions of the fraction 0.125, the extraction of manganese, cobalt, nickel and copper is 73.4%, 75.5%, 51.2% and 18.6%, respectively.

The study of the effect of the calcium chloride concentration on process indicators allowed us to conclude that, within the studied limits (600 - 900 g/l), it does not lead to significant changes in the extraction of valuable components. Therefore, it is preferable to work with calcium chloride concentrations of 600 - 700 g/l, because in this case, the density of the solution decreases and both the filtration of the pulp and the further processing of the solutions are simplified.
The study of the effect of concretion calcination at 105-500 °C on manganese extraction showed that with the increase in the calcination temperature, manganese extraction decreases: when using raw concretions, manganese extraction is 87.8%, and when using calcined concretions, it is 58.3%, which is associated with a decrease in raw materials porosity at the increase of calcination firing temperature.

The study of the effect of temperature and leaching duration on process indicators showed that temperature has a significant effect on the extraction of manganese, cobalt, nickel and copper from concretions. At a temperature of 180 °C, with an increase in the duration of the experiment from 1 to 3 hours, the extraction of manganese and cobalt increases. At 200 and 220 °C, a change in the duration of the experiment from 1 to 4 hours does not significantly affect the extraction rates of manganese and cobalt. With the increase in the temperature from 180 to 200 and 220 °C, the leaching rate of manganese and cobalt increases significantly. As a result, at 200 - 220 °C for 1 hour the same recovery is achieved as at 180 °C for 4 hours.

The temperature and duration of leaching are more difficult to influence on the dissolution of nickel and, especially, copper. This is due to the fact that iron sulfates for binding leaching products are consumed faster than non-ferrous metals dissolve. As a result, especially at elevated temperatures, hydrolysis of a part of the dissolution products, especially copper, is possible.

Table 1. The effect of temperature and leaching duration on the extraction of manganese, cobalt, nickel and copper from concretions.

| FeFeSO₄·7H₂O / Mnconc. | Experiment temperature, °C | Leaching time, h | Precipitation content, % | Precipitation analysis recovery, % |
|------------------------|-----------------------------|------------------|--------------------------|-----------------------------------|
|                         |                             |                  | Mn | Co | Ni | Cu | Mn | Co | Ni | Cu |
| 1.17                   | 180                         | 1                | 2.64 | 0.03 | 0.11 | 0.06 | 59.0 | 74.3 | 46.1 | 35.7 |
| 1.17                   | 180                         | 2                | 2.26 | 0.03 | 0.11 | 0.09 | 67.4 | 76.1 | 50.0 | 10.5 |
| 1.17                   | 180                         | 3                | 2.17 | 0.03 | 0.10 | 0.10 | 74.0 | 80.2 | 60.4 | 17.0 |
| 1.17                   | 180                         | 4                | 2.48 | 0.03 | 0.09 | 0.08 | 79.5 | 79.5 | 68.4 | 40.6 |
| 1.17                   | 200                         | 1                | 2.72 | 0.03 | 0.11 | 0.06 | 68.9 | 81.1 | 62.3 | 52.7 |
| 1.17                   | 200                         | 3                | 2.26 | 0.03 | 0.10 | 0.06 | 73.0 | 80.2 | 60.7 | 50.7 |
| 1.17                   | 200                         | 4                | 2.64 | 0.03 | 0.10 | 0.04 | 69.3 | 80.7 | 61.6 | 67.9 |
| 1.16                   | 220                         | 1                | 1.91 | 0.02 | 0.12 | 0.07 | 73.4 | 84.7 | 45.0 | 32.8 |

The most significant effect on the extraction of manganese, cobalt, nickel and copper is exerted by the mass ratio of iron in the form of sulfates to manganese in the charge. From the results shown in figure 1, it can be seen that the optimal ratio is in the range 1.25 – 1.35.

Thus, when using calcium chloride leaching with the sulfate iron (II) introduction into the solvent and the optimal parameters: temperature 180 - 220 °C; duration 1 to 3 hours; the concentration of calcium chloride in the initial solution 600 – 700 g/l; fineness of concretions less than 0.125 mm; FeFeSO₄·7H₂O/Mnconc. 1.25 – 1.35, 81.0 – 88.0% Mn, 78.0 – 85.0% Co, 51.6 – 68.4% Ni, 40.6 – 51.0% Cu.

Figure 1. Effect on the manganese extraction of the mass ratio of iron (II) in sulfates to manganese in concretions.
The use of aqueous solutions of iron chloride (table 2) allows up to 99.2% of manganese to be extracted, with the extraction of cobalt up to 99.1%, nickel up to 82.7%, copper up to 73.8%.

**Table 2.** The effect of the mass ratio of iron (II) in chlorides to manganese in concretions on the extraction of manganese, cobalt, nickel and copper.

| FeFeSO₄.7H₂O / Mnconc. | Extraction, % |
|------------------------|--------------|
|                        | Mn | Co | Ni | Cu |
| 0.56                   | 18.80 | - | 54.57 | 61.04 |
| 1.11                   | 71.08 | 51.34 | - | - |
| 1.65                   | 98.83 | 93.75 | 65.75 | 71.72 |
| 2.19                   | 99.19 | 99.15 | 82.77 | 73.80 |
| 2.74                   | 99.25 | 99.28 | 71.38 | 58.73 |

For experiments on the leaching of valuable components from polymetallic ores, the ratio of iron (II) in chlorides to manganese in the ore equal to 1.65 was used. The experimental results in table 3 show that as for the extraction of manganese, nickel, cobalt and copper, they are in the same range as in the FMC leaching.

The resulting concentrate is characterized by high quality, especially in its content of phosphorus, sulfur and silica and contains 55 – 64 % Mn; 0.1 – 2.31 % SiO₂; < 0.55 % Fe; < 0.073 % S and < 0.005 % P. When using hydrochloric acid as a solvent to neutralize its excessive amount, carbonate manganese ore was used.

**Table 3.** Indicators of extraction of manganese, cobalt, nickel and copper from polymetallic manganese ore.

| Test No. | Precipitation analysis recovery, % |
|----------|-----------------------------------|
|          | Mn | Co | Ni | Cu |
| 1        | 95.35 | 78.50 | 55.22 | 62.42 |
| 2        | 98.83 | 93.75 | 65.75 | 71.72 |
| 3        | 99.17 | 97.76 | 74.79 | 68.97 |
| 4        | 99.19 | 99.15 | 82.77 | 73.80 |

It is advisable to maintain the ratio of HCl_pr/HCl_theor in the range of 1.9 – 2.80, and the process temperature in the range of 85 – 95 °C. At a concentration of HCl in the solution of 200-300 g/dm³, metals leaching is carried out in 70-120 minutes. The neutralization of the excess amount of hydrochloric acid was carried out by carbonate ore with different manganese contents (12.95 and 29.8%). From the solution of carbonate ore passes from 48.2 to 95.4 % Mn.

Residues from carbonate ore during neutralization, containing about 7% Mn, can be used in the initial stage of neutralization.

Precipitation of non-ferrous metals, Co and Ni from solution using sodium sulfide or hydrogen sulfide allows high extraction of metals from raw materials to be achieved. Manganese hydroxide is precipitated from the solution by hydrolysis at pH 2 – 3. From the purified solution – at pH 8.5 – 9.0. Extraction of non-ferrous metals in the solution is 99.80 – 99.88%. Manganese concentrate obtained from manganese hydroxide by calcination contains up to 60% manganese and less than 0.005% phosphorus.

All products of FMC processing according to these methods are suitable for use. Manganese concentrate is a raw material for the production of manganese alloys, iron ore material is used for the production of agglomerate and metallized iron, and non-ferrous metal concentrate is used for the production of cobalt and nickel [5].
4. Conclusion
The introduction of ferrous manganese concretions into the chlorine-calcium enrichment process allows the extraction of manganese to be increased by 2.3, cobalt by 3.2, and nickel by 2.5 times. During processing of raw ferromanganese concretions and polymetallic ores, non-ferrous metals are also well recovered: 98-99 % Co; 83-98 % Ni; 74 % Cu at 95-99 % Mn. As a result, it is possible to obtain manganese, copper-nickel-cobalt and iron concentrates. Leaching of FMC with an aqueous solution of hydrochloric acid with neutralization of its excessive concentration by the introduction of carbonate manganese ore makes it possible to extract non-ferrous metals in a solution of 99.80 – 99.88% and up to 95.4% Mn.

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