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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Improvement of Technology for Producing Pure Pyrolusite from Carbonate Ores

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1. INTRODUCTION

World reserves of manganese ore are estimated by 3.46 billion ton that includes 2.54 billion ton in the former Soviet Union. Deposits of manganese ore are distributed unevenly on the territory of the former USSR. In Ukraine is concentrated 82.4% of the total reserves of manganese ores, in Georgia 8.9%, in Kazakhstan 2.6%, the share of Russian Federation is 6.1%. The ore deposits of the Russia almost entirely represented by carbonate and carbonate-silicate-oxide forms of a very complex mineralogical composition [1].

High peroxide and oxide ores available in limited quantities in Georgia and Ukraine (Chiatursky and Nikopolsky pools), to 1990 were mostly consumed.

According to plans of USSR Ministry of Ferrous Metallurgy (Minchermet), the main consumer of the manganese ore, planned further increase of its production basing mainly on the processing of carbonate ores. These ores are not appropriate for obtaining concentrates with low content of phosphorites using physical and mechanical methods according to the technological schemes of the existing processing factories. Increase in the share of the carbonate ore at the producing manganese concentrates leads to a deterioration in their quality due to low yield of manganese and high content of phosphorus, silica and other impurities. To maintain the quality of manganese concentrates on the level of requirements of ferroalloy and other metal industries, already since 1983 was necessary to import 180–230 thousand ton/year of peroxide high-manganese ore (MnO_2) from Australia, Gabon, Canada, Brazil. This ore was used in domestic factories as additive to concentrates. Despite this, it was impossible to avoid decrease in the techno-economic indicators both at the stage of mining and in metallurgical process [2].

Reduction in the quality manganese concentrates adversely affected also another customers, the chemical industry, that produces chemicals and pure manganese compounds for electronics. This led to complication of technologies for producing manganese compounds, to increase in the amount of waste in the form of sludge, aggravates the ecological situation. It should be stressed that it was for environmental reasons that were closed several plants of manganese compounds, for example, the production of potassium permanganate in the town of Saki (Crimea), the production of manganese nitrate as chemical in the St. Petersburg and others.

Currently, Russian Federation has a very unfortunate situation with the industry of manganese raw material. This is a result of a number of reasons, one of which is the lack of proper attention to its own raw material base in respect of manganese, owing to the existence until recently of powerful sources of the raw material in Ukraine, Georgia, and Kazakhstan. Production of manganese compounds and concentrates of manganese for the metallurgy was created predominantly at the existing mining and concentrating enterprises, located predominantly near the sources of raw materials. After the collapse of the Soviet Union, this led, in particular, to the shortage of production in Russia of many manganese compounds, such as potassium permanganate, electrolytic and chemically produced manganese dioxide, reactive salts for electronics, despite the fact that respective technologies have been developed largely by Russian organizations.

As an example can serve the technology for producing high-purity pyroluzite from the manganese ore of any type by nitrate method developed by State Institute of Applied Chemistry in St. Petersburg (NPO GIPH) in 80–90th of the last century.

By order of the USSR Minchermet was developed a variant of technology based on carbonate ores of Nikopol deposits for producing pyrolusite with the production capacity 150 thousand ton/year at the Marganets mining and enrichment plant (Ukraine). However, because of well-known social and political changes and the collapse of the Soviet Union the production has not been created.

For Russia, the development of industrial technology of chemical enrichment of manganese ore is extremely important, however, establishing of large scale production of pyrolusite in relation to the mining and enrichment plants in the short term is hardly possible. This is due to the poor developed of domestic deposits and poor infrastructure. A more realistic is another way: the crea-tion of a relatively small (with capacity 10–20 thousand ton per year of pyrolusite) modules on both complex domestic and imported ores, not necessarily related to the mining and enrichment plants. From a viewpoint of high-scale iron and steel industry such modules would be insignificant, but they would enable acceleration of development of the production of pure manganese compounds for chemistry and electronics on a new basis.

2. FORMULATION OF PROBLEM

Analysis of technology developed for large scale production in the mining and enrichment plants showed that a number of technical and technological solutions can not be used in the creation of a separate production of modular design.

In the version of technology developed for Marganets mining and enrichment plant is used the countercurrent process of the ore leaching which leads to formation of sludge of two types: with large particles of sand type (mainly, SiO_2, MnO_2) and fine clay slurry. The latter practically does not lose water and therefore after purification from nitrates and biological denitration to maximum allowed concentration is transformed into a slurry (pulp) with a mass ratio of liquid/solid about 7 which commonly is out to the plant slurry field.

It is obvious that such an option is acceptable only for mining and dressing enterprises which have slurry field while at the organization of production in the absence of such field the pulp withdrawal becomes a great disadvantage of technology hindering its implementing by the environmental reasons.

Therefore, it is necessary to design the technology with the withdrawal of the sludge in a dry form, with the possibility of its eventual utilization for producing building materials. Such approach has been already tested on the same sludge in several research institutions, including GIAP (State Institute of Nitrogen Industry), Moscow.

At the processing of carbonate ores (and, in particular, from the Russian ore deposits) with nitric acid are formed solutions with the mass ratio of Ca and Mg nitrates is 5 or higher. With such a ratio of Ca and Mg in the solution, as will be shown below, the long-term maintenance of the thermal decomposition of manganese nitrate is impossibl6e.

In the present paper is described a method of nitrate-based chemical enrichment of manganese ores and the results of studies on the development of a technology free from the above-mentioned disadvantages.

3. CHARACTERISTICS OF NITRATE METHOD OF CHEMICAL ENRICHMENT OF MANGANESE ORES

The nitrate method developed in the Scientific center “Applied Chemistry” (formerly GIPH) is based on the extraction of manganese and related elements into solution in the form of nitrates, purification of the solution to remove the compounds of iron, aluminum and phosphorus, its concentrating by evaporation and isolation of the final product of ore dressing by thermal decomposition of manganese nitrate in the presence of nitrates of calcium, magnesium, potassium and sodium, in correspondence with the equation:

$$Mn(NO_3)_2 \rightarrow MnO_2 + 2NO_2. \quad (1)$$

The method is suitable for processing the ore of any type. In the case of oxide ores the dissolution (leaching) of MnO_2 is performed with circulating nitrogen oxides produced in the reaction (1) at the thermal decomposition of $Mn(NO_3)_2$, dissolution of MnO with reverse nitric acid synthesized from the nitrogen oxides and industrial water or with the nitric acid introduced into the process from external source. In the latter case there is a possibility of obtaining as a commercial product not only artificial pyrolusite (β-MnO_2) but also pure manganese nitrate solution through the dissolution of the resulting manganese dioxide with nitrogen oxides.

In the case of carbonate ore whole manganese is extracted into solution using returned nitric acid.

At the processing of the ore of any type by the nitrate method should be introduced fresh nitric acid in the quantity required for the dissolution of compounds of alkaline earth metals (Ca, Mg) and oxides of alkali metals (K, Na). In the nitrate method developed in the Center of Applied Chemistry the extraction into the solution of alkaline and the alkaline earth metals is crucial.

As the acid to dissolve compounds Ca, Mg, K, Na is introduced additionally, the corresponding part of the solution of nitrates of these elements should be removed from the production line and processed into liquid or granular fertilizer on the basis of calcium nitrate.

4. RESEARCH ON THE DEVELOPMENT OF A VERSION OF THE CONCURRENT MODE LEACHING THE ORE WITH THE WITHDRAWAL OF DRY SLUDGE

4.1. Concurrent (Single Step) Leaching

It was found that the concentration of acid in a wide range (from 3–5 to 30%) practically does not influence the rate of extraction of components of the carbonate manganese ore under the condition of good contact of solid and liquid phases (stirring).

In the range of small concentrations of acid (about 3%) to maintain acceptable, in the terms of technology, rate of the process is required initial grinding of ore. It was shown that at the grinding ore to the particle of about 1 mm size the increase in the process rate provides attaining the maximum possible degree of extraction of components from the ore for about 1 h at a temperature of 45 to 50°C and reliable fluidization of the ore. The residual acidity is not higher than 0.1–0.2% of the totally loaded acid (pH in the range of 1 to 1.5), and extraction of the main elements of the ore are as follows: Mn 88.1%, Ca 98.4%, Mg 72.6%, K 89.6%, Na 83.8%. These data are very similar to the results of leaching in countercurrent mode (88.5%, 98%, 72%, 90% and 90%, respectively). The unreacted sludge (dry substance) is 26.8% of the mass of the loaded ore.

During the leaching, the solid phase particle size decreases from the maximum (1 mm) and the ratio by weight liquid/solid of the pulp increases from 6.2 to 14.6. This pulp can be reliably weighted in the apparatuses with conventional stirring devices (such as anchor stirrer) and moved along the chain of technological units as a fluid. This opens up a possibility of using relatively inexpensive standard devices instead of countercurrent tubular leaching apparatus of specific design.

The results obtained showed that the preliminary crushing of ore and reliable weighing in a solution of salts allows to perform the leaching process in the concurrent (single pass) mode, with formation of sludge of one type.

4.2. Separation of Sludge from the Solution, Washing it from Salts and Dehydration

Environmentally safe technology should include the separation of sludge from the solution, almost complete washing off the salts and dehydration of sludge to allow its subsequent application in the production of building materials.

In the nitrate technology is adopted the most economical way of the sludge separation from the solution by settling in the thickener in the presence of flocculants (polyacrylamide). The rate of the sludge thickening is affected by the degree of dilution of the original pulp (mass ratio liquid/solid), by consumption of flocculants (kg per 1 ton of sludge), by the contents of acids and salts in solution. It was found that the optimal consumption of flocculants for the nitrate solutions at processing carbonate ore (mass fraction of salt is about 36%) is about 0.7 kg/ton, and it little depends on the degree of dilution of the original pulp and acid content in the solution.

The degree of dilution of the pulp has a major effect on the rate of thickening the sludge, especially for thin clay slurry obtained by countercurrent leaching. For such pulp the liquid/solid ratio should be at least 40 to obtain a suitable for the technology rate of thickening (1.5 m/h).

We found that the sludge produced at the concurrent leaching can be much better concentrated, probably due to the presence of relatively large porous particles that can carry the clay fraction of sludge. Even at the ratio liquid/solid of about 15 the thickening rate was not less than 1.6 m/h, and the ratio liquid/solid in the condensed sludge equals approximately 2 instead of 7–8 in the clay slurry.

In this case, the rate of sludge thickening is affected also by the value of pH of the solution: in the weak acid solution with pH 1–1.5 it was about twice higher than in the solution neutralized to pH 3.5–4. This is important, because twofold increase in the rate of sedimentation allows 1.4 times reducing the estimated diameter of thickener.

This technology includes enhancing the pH of solution after leaching for its purification from compounds of iron, aluminum, phosphorus, etc., extracted from the ore into solution. In principle, the degree of purification of the solution from these compounds by increasing its pH may depend on the presence or absence of sludge in the system. However, at the recommended conditions of purification of solution (temperature 80–90°C, maintaining at pH 4 for about 1 h) that was not found. According to atomic absorption analysis of trace mass fraction in the solution neutralized with clay slurry the content of contaminants is: Fe 0.0005%, Al 0.0002%, Co 0.0002%, Ni 0.0014%. The corresponding figures obtained for the clarified solution: 0.0004%, less than 0.0002%, less than 0.0002%, less than 0.0014%.

According to the data the initial separation of the pulp followed with neutralization is useful to reduce the size of thickener.

Washing off the salt from the condensed sludge is carried out by countercurrent decantation in a cascade of thickeners. The method is applied on an industrial scale, and calculations of the cascade parameters are well known.

At the investigation of the possibility of dehydration of washed from salt sludge by filtration is found that the ore sludge is filtered much better than the clay slurry. The rate of filtering on the filtrate at a pressure drop on the filter 0.07 MPa and the height of the layer of sediment about 1 cm was 116 $dm^3\,m^{-2}\,h^{-1}$). After pressing the sediment on the filter at the above specified pressure for one the minute its humidity was around 25%.

The composition of sludge (per dry substance): MnO 2.14%, MnO_2 9.74%, SiO_2 73.28%, oxides of Ca, Mg, K, Na, Al, Fe, etc. 13.1%, polyacrylamide 0.1% , $Fe(OH)_3$ 0.45%, $Al(OH)_3$ 0.21%, $FePO_4$ 0.03%, $CaCO_3$ 0.5%, $MgCO_3$ 0.42%, nitrates less than 0.03%.

5. OPTIMIZATION OF THE PROCESS OF THERMAL DECOMPOSITION OF MANGANESE NITRATE

As already indicated above, at the nitrate technology, it is important to conduct thermal decomposition of manganese nitrate in the presence of nitrates of Ca, Mg, K, Na, as in this case does not occur the complete dehydration at the temperature of up to 200°C and is formed capable to flow suspension of manganese dioxide in a solution of salts with a relatively low temperature of solidification which can be easily removed from the reactor.

To calculate the equilibrium mass fraction of manganese nitrate at its thermal decomposition in [3] is suggested an equation:

$$C_p = A_0 - AT - BX + XT^nY, \quad (2)$$

where T is absolute temperature by Kelvin, A_0, A, B, C are constants; X, Y are dimensionless parameters reflecting the composition of the solution of alkali and alkaline earth metal nitrates: X = mass fraction of $Ca(NO_3)_2$ /sum of mass fractions of $Ca(NO_3)_2$ and $Mn(NO_3)_2$; Y = the sum of the mass fractions of KNO_3 and $NaNO_3$ / sum of mas fractions of $Ca(NO_3)_2$ and $Mn(NO_3)_2$.

Since the macro-contaminants in the solution of the manganese nitrate obtained from ore are Ca and Mg nitrates (the nitrates of alkaline metals approximately by an order of magnitude below), temperature and the ratio of Ca and Mg nitrates in the system (parameter X) exert the main influence on the equation (1).

The main researches on nitrate technology were performed with the oxide-carbonate ores of Nikopol deposits with carbonate contents of up to 20%. For the solutions obtained from these ores, the value of X decreases to the range 0.3–0.5. It was found in [4] that at this ratio of Ca and Mg nitrates in the system the activation energy of reaction (1) is minimum. Also important is the fact that with the specified X values flowing melt of the salts formed, crystallization MnO_2 took place mainly in the volume of apparatus, and the specific rate of depositing the product on the details of the device (mainly on the heating surface) did not exceed 5–6 g MnO_2 / m^3 h.

At processing carbonate ores are obtained other values for X, 0.8 and above. Our study showed that the increase of calcium content in the system negatively affects the process of thermal decomposition of manganese nitrate.

First, at the increase in viscosity and temperature of freezing the salt melts, the conditions of heat transfer into the reaction mixture bulk deteriorate resulting in lower degree of decomposition of manganese nitrate and crystallization of MnO_2 mainly on the heating surfaces. At higher content of calcium nitrate in the system (X = 0.9 and above) the melts with the freezing temperature about 150°C are obtained, and at the working temperature of 175–180°C (as adopted in the nitrate technology) they can not be unloaded from the reactor.

Secondly, it is found that under the conditions of thermal decomposition of manganese nitrate, calcium nitrate is able to crystallize; it is deposited and promotes deposition of MnO_2 on the reactor parts (mechanical co-precipitation)

It is shown below the dependence of temperature of the start of deposition of $Ca(NO_3)_2$ crystals (*T*єC) on the ratio of nitrate Ca and Mg in the salt melt (parameter X):

X	0.3	1	0.67	0.75	0.8
T°C	172	162	157	154	152

The data show that in order to practically exclude crystallization of $Ca(NO_3)_2$ at operating temperatures (170–190єC), the value X in the system should be 0.3 or below. At the processing oxide and oxide-carbonate ore this condition is approximately fulfilled (X ~ 0.5). It is useful at the processing of carbonate ores to add to the initial manganese ore some minerals, such as dolomitized magnesite from 1 kg of which at the processing with nitric acid is produced, 1.55 kg of $Mg(NO_3)_2$, 0.2 kg of $Ca(NO_3)_2$ and 0.3 kg of sludge. It should be added in a quantity necessary for providing after the leaching the content of Ca and Mg nitrates in the desired ratio (the value of X less than 0.5). Adding magnesium to the system is useful also in another respect: it increases the value and efficiency of agrochemical liquid fertilizer formed at the producing pyrolusite.

CONCLUSIONS

(1) Pre-grinding carbonate ore to the particle size of about 1 mm is used to perform the process of leaching in concurrent (single pass) mode using standard device with stirrer of relatively low cost.

(2) Leaching in the concurrent regime simplifies considerably utilization of side products as one type of sludge is formed rather than two in the countercurrent mode.

(3) At the separation of sludge from the acid salt solution (before neutralization) the rate of its sedimentation increases twofold that allows 1.4-fold decrease in the diameter of the thickeners.

(4) The main sludge formed at the concurrent regime of leaching unlike the thin clay slurry obtained in the countercurrent mode can be dehydrated at filtration, and removed from the production in the dry state, and then used in the production of building materials.

(5) Mixing the original ore with the dolomitized magnesite optimizes the composition of the medium at the thermal decomposition of manganese nitrate and ensures efficiency of the reactor of thermal decomposition.

(6) The technology including the above-mentioned solutions enables arrangement of the independent production of manganese oxide, in part, outside the mining and enrichment enterprises.

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