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# DESIGN OF A HYDROMETALLURGICAL COMPLEX FOR PROCESSING OF COMPLEX LOW-GRADE MANGANESE ORES

D. Yu. Zhukov<sup>1</sup>, Yu. M. Averina<sup>1</sup>, V. V. Menshikov<sup>1</sup><sup>1</sup> D. Mendeleev University of Chemical Technology of Russia (Moscow, Russia)

E-mail: averinajm@mail.ru

## AUTHOR'S INFO

**D. Yu. Zhukov**, Dr. Eng., Adviser to the Rector,  
**Yu. M. Averina**, Dr. Eng., Associate Professor, Dept. of Innovative Materials and Corrosion Protection,  
**V. V. Menshikov**, Dr. Eng., Professor, Dept. of Innovative Materials and Corrosion Protection

## Key words:

Manganese, manganese ore, pyrometallurgy division, leaching, chemisorption, nitrate method.

## ABSTRACT

This paper describes a sulfuric acid leaching technique applicable to complex low-grade manganese ores. The technique helps to obtain manganese sulfate solutions, which are further subjected to electrolysis and chemisorption. The final products of the above processes include conforming commodities, as well as primary products for pyrometallurgy, i.e. a mixture of bi- and quadrivalent manganese oxides. The paper also describes a technique for obtaining synthetic pyrolusite from nitrate solutions, which is a pure  $\beta$ - $\text{MnO}_2$ . The nitrate technique is applicable to any kind of manganese ores, including manganese oxide ores, manganese carbonate ores, and complex ores. This technique offers a feasible comprehensive solution for producing concentrates which can be further processed to produce manganese metal and low-carbon ferroalloys. The paper contains detailed diagrams and material balances of the processes and lists the equipment that would be necessary to implement these techniques. Target products and by-products are listed separately. Sanitary restrictions and waste products are also mentioned in the paper.

## Introduction

This paper describes a competitive hydrometallurgical technique to produce high-quality manganese products from complex low-grade manganese ores. A competitive advantage of this technique is in the high quality of the final products versus their production cost. This indicator takes this technique beyond competition. The obtained target products, which are of value in metallurgical and chemical industries, have a wide range of application. Thus, they can be used in the production of alloying additions for steel industry, the latter can be used in the production of manganese metal [1], due to which the through ore-to-steel transition of manganese can be doubled. This makes it possible to cut twice the wastes associated with manganese ore extraction without affecting steel output. Should this technique see a successful implementation, it will potentially lessen Russia's dependence on the global manganese market [2–5].

The goal of the research is to design a hydrometallurgical complex. This complex is designed to tackle the following tasks [6–8]:

- 1) Leaching of manganese ore samples to produce manganese sulfate and nitrate solutions;
- 2) Obtaining from manganese sulfate solutions:
  - Electrolytic manganese dioxide (hereinafter referred to as 'EMD', final conforming product);
  - Electrolytic manganese metal (hereinafter referred to as 'EMM', final conforming product and commodity);
  - Chemisorption manganese oxide complex (hereinafter referred to as 'CSC', which serves as the primary

product for the subsequent pyrometallurgical process and for chemical industry);

- 3) Production of synthetic pyrolusite (from nitrate solutions), which is a pure  $\beta$ - $\text{MnO}_2$  (hereinafter referred to as 'SPYR', which serves as the primary product for the subsequent pyrometallurgical process and for chemical industry).

## Sulfuric Acid Leaching

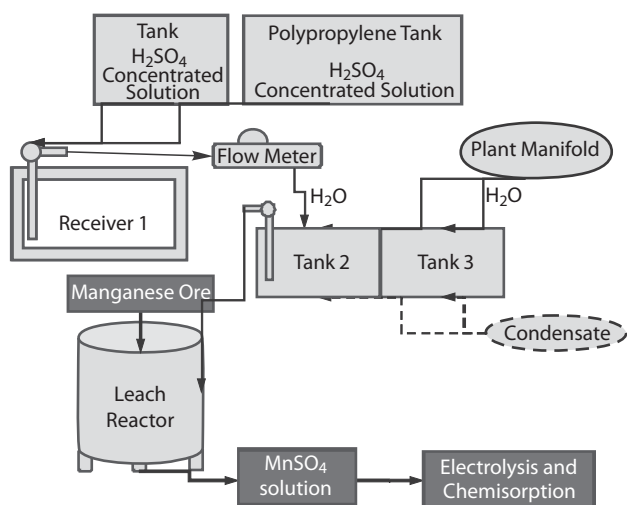
Through the use of sulfuric acid for leaching manganese ores, it is possible to obtain manganese sulfate solutions and slime waste [9]. Manganese sulfate solutions are then sent to electrolysis and chemisorption lines. A sulfuric acid leaching line consists of: an acid storage and preparation yard (25% sulfuric acid solution); a leach reactor; a manganese sulfate tank; and a slime pit.

Sulfuric acid leaching of manganese carbonate ore, manganese slags and ferromanganese concretions produces a 23–25% manganese sulfate solution, from which manganese sulfate crystals are produced through further hydrometallurgical process or electrolysis. Resultant slimes are used in the production of construction materials.

**Material balance.** The components include manganese ore — 0.64, 100% sulfuric acid — 1, product — manganese sulfate.

**Manganese ore.** Manganese carbonate ore from Russian deposits, manganese slags and ferromanganese concretions of any compositions after physical and mechanical preparation in the first section. Required concentration:  $35\% < \text{Mn} < 7\%$ , size: 2 mm.

**Sulfuric acid**  $\text{H}_2\text{SO}_4$  (GOST 5760-79). Specification: Molecular weight — 98.08, boiling point =  $330^\circ\text{C}$ , density



**Fig. 1. Block diagram: sulfuric acid leaching of manganese ore**

at 20 °C — 1.839 kg/m<sup>3</sup> at 80%, 1.200 kg/m<sup>3</sup> at 23%, melting point = 8.48 °C, MPC = 1 mg/m<sup>3</sup> (hazard class 2).

**Sanitary restrictions.** When mixed with water, it generates a lot of heat. It may irritate upper airways. When in contact with skin, it may cause a strong burning pain and actual burns.

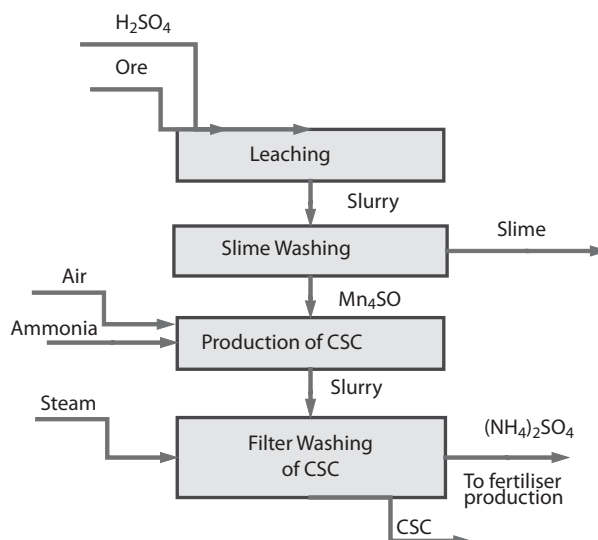
**Result of leaching.** 23–25% MnSO<sub>4</sub> solution, which goes to further hydrometallurgical process and electrolysis or to vaporization to become manganese sulfate crystals with the following characteristics: Molecular weight of anhydrous MnSO<sub>4</sub> — 156, density of anhydrous MnSO<sub>4</sub> — 3.25 g/cm<sup>3</sup>, melting point of anhydrous MnSO<sub>4</sub> = 700 °C, MPC = 2 mg/m<sup>3</sup> (hazard class 2 in water). Non-explosive.

**Waste products.** Slimes — Slimes can be used in the production of construction materials. The principal diagram of the process is shown in **Fig. 1**.

Concentrated sulfuric acid is delivered in a tank truck or in polypropylene tanks and is dumped in Receiver 1. From the receiver, through a flow meter, small portions of sulfuric acid are fed in Tanks 2 and 3, which contain certain amounts of portable water and condensate delivered from the plant manifold. A thermocouple controls the temperature and once the threshold point of > 30 °C is reached, the receiver stops feeding acid. A submersible pump feeds the diluted 25% sulfuric acid to the leach reactor via a flow meter. Manganese ore after physical and mechanical treatment is also fed to the reactor. The resultant product includes a 23–25% MnSO<sub>4</sub> solution, which is collected in a tank and from there goes to electrolysis and chemisorption stages.

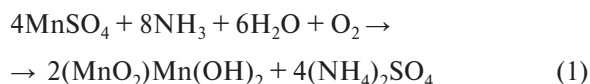
### Chemisorption

The chemisorption process (**Fig. 2**) includes a process of manganese sulfate oxidation with air producing a chemisorption complex (CSC); washing, drying and packaging of CSC, and production of fertilisers from ammonium sulfate solution.



**Fig. 2. Block diagram: chemisorption process**

The theoretical basis of the above process is described in papers [1, 10–12]. After prior concentration, carbonate ore is oxidized with air in the presence of ammonia liquor in chemisorption reactors to produce a chemisorption manganese complex, which can then be processed to become active manganese dioxide, pure manganese salts, potassium permanganate, etc. or manganese metal. The following formula describes the chemisorption complex production process:



The chemisorption line is comprised of tanks for MnSO<sub>4</sub>, ammonia liquor, ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, condensate; a CSC yard, which consists of a CSC reactor, an air blower, a thickener, a filter press and two Nutsche filters and drying, grinding and packaging sections. The chemisorption line also includes a by-product section, which consists of a rotary evaporator, an evaporation dish and an absorber.

**Ingredients and products:** 23–25% MnSO<sub>4</sub> solution, which is a product of the leaching line. Ammonia liquor NH<sub>4</sub>OH (GOST 3760-79): Molecular weight — 17.03, density — 907 kg/m<sup>3</sup>, MPC (ammonia) — 20 mg/m<sup>3</sup> (hazard class 4).

Ammonia liquor produces the same effects as the ammonia that precipitates from ammonia liquor solutions. Ammonia liquor is not flammable and does not pose explosion risks when stored in open containers or if spilt.

**Products:** CSC. Formula — Mn<sub>2</sub>O<sub>3</sub> (dark brown to black powder, insoluble in water). Mass concentration of Mn — 67%. Not flammable or explosive. Hazard class 2. MPC in workplace air = 0.3 mg/m<sup>3</sup>.

**By-products:** 23% ammonium sulfate solution. After condensation to 35%, the solution becomes a seasonal marketable product. When concentrated to form crystals, it becomes a commodity with the following specification: Ammonium sulfate anhydrous (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (GOST

Table 1. **Material balance of the chemisorption process per 1 ton of product**

Reactants	Input, kg	Concentration	Consumed, kg	Output, kg	Concentration	Losses, kg
MnSO <sub>4</sub> [manganese sulfate solution]	3500 <sup>1</sup>	27%	3480			20
NH <sub>4</sub> OH [ammonia liquor]	3000 <sup>2</sup>	27%	3000	0		
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> [ammonium sulfate]				3000	24%	
MnO <sub>2</sub> ·Mn(OH) <sub>2</sub> [CSC]				2000 <sup>3</sup>	100%	
Total sulfates [K, Na, Mg]	50			50		
H <sub>2</sub> O	11600		11000			600
O <sub>2</sub>	370 <sup>4</sup>					

Notes: <sup>1</sup>945 kg of dry MnSO<sub>4</sub> or 1,890 kg of manganese sulfate monohydrate; <sup>2</sup>800 kg of NH<sub>3</sub>; <sup>3</sup>Solid phase%; <sup>4</sup>3.1 th m<sup>3</sup> of air,  $d = 1.3 \text{ kg/m}^3$ ,  $G_{\text{in}} = 23.2\%$ ,  $G_{\text{out}} = 14.0\%$

Table 2. **Manganese oxide CSC characteristics**

Indicators	Values, %
Weight fraction of manganese (Mn)	minimum 67.00
Weight fraction of phosphorus (P)	N/A
Weight fraction of sulfur (as requested by customers)	0.05–0.3
Dispersity	A wide range of grain sizes, as agreed with the customer
Hydroscopic moisture	3
Crystal moisture	4

9097–82). Molecular weight — 132.13, density of the 23% solution — 1,150 kg/m<sup>3</sup>. MPC = 10 mg/m<sup>3</sup> (hazard class 3 in water). Solubility in water: at 25 °C — 46.30%, at 100 °C — 50.42%. Not flammable or explosive.

**Waste products:** Neutralized ore slime (suitable for the production of construction materials). Filtrate is pumped from the filter presses into a tank, in which the concentrated manganese sulfate solution from the first slurry pressing stage is blended with industrial water. The manganese sulfate solution and the circulating water contain 3 to 5 grams of sulfuric acid per liter. These solutions are neutralised in the tank through small additions of ammonia following stoichiometry. The mixing is performed by a recirculation pump. The required concentration in the tank is achieved through the addition of primary manganese sulfate solution with a higher concentration (30–35%).

This is a closed loop process with no liquid waste produced. Ammonium sulfate finds application in agriculture as a nitrogen fertilizer.

The MnSO<sub>4</sub> solution coming from the leach reactor is pumped in a tank, in which it is mixed with water at the first stage. After that, a filtrate arrives from the filter press, i.e. a recirculation MnSO<sub>4</sub>. The NH<sub>4</sub>OH and MnSO<sub>4</sub> solutions are fed from the storage tank and the process tank correspondingly into the reactors. They travel through gage tanks, and the amounts fed are controlled by flow meters.

An air blower supplies air to the reactor in the amount that is necessary to support a reaction with oxygen; the recirculation MnSO<sub>4</sub> solution is pumped into the gage tank.

The main reactor is running continuously. Once a certain level has been reached, the product flows to the downstream reactors. These two reactors activate at regular intervals and run as long as there is MnSO<sub>4</sub> in them. Ammonia leaves the reactors with vent emissions; the concentration of ammonia can reach up to 200 mg/m<sup>3</sup>. That is why the vent is directed at an absorber filled with water. If the concentration of NH<sub>3</sub> > 200 mg/m<sup>3</sup>, the NH<sub>4</sub>OH feed to the reactors is cut off; when the concentration of NH<sub>3</sub> < 100 mg/m<sup>3</sup>, the shut-off valves open up. The resultant CSC, mixed with ammonium sulfate, is pumped into the thickener for separation.

From the bottom of the thickener, the CSC slurry is pumped into a receiver, and from there onto the filter press. Air is used to push the slurry from the receiver to the filter press —  $P = 6 \text{ kgf/m}^2$ . The pressed slurry is re-pulped and fed to the Nutsche filters. Wash condensate is fed to the Nutsche filters as well. Filtered and washed CSC (which has a texture of thick paste) goes for shelf drying. The CSC is placed on pans and is dried at 100 °C with hot air generated by a fan heater. To stop dust from spreading in the building, the shelf with the pans is placed in a fume hood with a filter.

From the top of the thickener, the ammonium sulfate is pumped in the tank. From there it is fed to the by-product line, where it is concentrated to a 35% solution or evaporated to crystals.

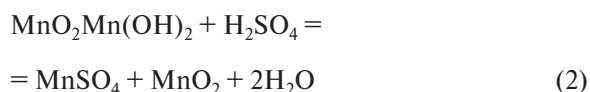
From the by-product line, the condensate comes in the tank. A portable submersible pump then delivers the condensate to the washing section and to the absorber for ammonia recovery. All excess condensate goes to the leaching section and is used to dilute sulfuric acid in the tanks. Thus, the environmental impact of this process is minimized.

The filtrate from the Nutsche filters and the filter press is pumped to the rotary evaporator. A vacuum pump equipped with a vacuum trap generates vacuum for the Nutsche filters.

The aim of the process control is to bring the material balance to zero, as expressed by the chemical reaction, by adjusting the feed of the reagents, including manganese sulfate, ammonia, and oxygen. The material balance of the chemisorption process given per 1 ton of the finished

product is shown in **Table 1**. **Table 2** describes the resultant CSC.

The resultant chemisorption complex of manganese oxides is a valuable semi-product, which is a mixture of bi- and quadrivalent manganese oxides. Active manganese dioxides can be produced when the CSC is treated with sulfuric acid. This process takes place in a reactor and can be described with the following formula:



The active manganese dioxide reactor runs at intervals, three leaching cycles every 24 hours. Portions of thickened slurry are pumped in the reactor from the thickener.

After that, 23–25% sulfuric acid is fed to the reactor. For a quality product, the acid should be fed gradually in the course of an hour. When the pH level in the reactor reaches  $5 < \text{pH} < 6$ , the last portion of acid is fed at the ratio of 5–7 g/l. After 15 minutes in the reactor, the mixture is delivered to the filter presses and is then washed, dried and packaged. The active manganese dioxide slurry is pumped onto the filter press by a 6 atm slurry gear pump. Compressed air can be used for additional product pressing. Through acid treatment the product is separated into pure salt and active manganese dioxide  $\gamma$ -crystals. The CSC can be easily processed to become active manganese dioxides (AMD), pure manganese salts, potassium permanganate, etc. The CSC can also be used to produce a high-quality manganese metal. Due to chemisorption process, active manganese dioxides have an exceptionally large specific surface area, so they can make excellent catalysts and can be used in the production of electric cells. Active manganese dioxides can partially substitute electrolytic manganese dioxides or can be an addition to the latter. Besides, as mentioned above, the CSC can be used to produce high-quality manganese metal and ferroalloys.

### Nitrate Method

The nitrate method can and should become a driving force of Russia's manganese industry as it can be deployed on a grand scale with over a hundred thousand tons of synthetic pyrolusite (SPYR) produced every year. In quality terms, this product surpasses any natural ore while having a comparable cost.

The main advantages of the nitrate method include: the possibility to use not only low-grade manganese ores with the manganese concentration of no less than 18% and any impurities (including riddlings and dumps) but also wastes generated by ferroalloy industry; environmental friendliness of the process, no hazardous tailings or wastes; valuable by-products; good filterability of intermediate and final products, closed-loop water system.

The differential advantages of this method make a key integral indicator reflecting quite a positive quality-

Table 3. SPYR composition	
Components	Weight Fractions
MnO <sub>2</sub>	99
Mn <sub>general</sub>	62.6
SiO <sub>2</sub>	0.2
S	0.02
P	<0.005
Σ (K, Mg, Na, Ca)	<0.25
Humidity	3

cost correlation, which takes this method beyond competition.

SPYR, the key product of the nitrate method, is a coarse-crystalline well-crystallized  $\beta$ -MnO<sub>2</sub> with a vanishingly low concentration of phosphorus and sulfur and the total concentration of impurities under 1%. It looks like a silver powder with the dispersity of 40 — 100  $\mu\text{m}$  and the bulk weight of 2.4 g/cm<sup>3</sup>. SPYR is a valuable material for metallurgical and chemical industries (**Table 3**). Because it can be used to produce manganese metal and alloying additions for steel, the through ore-to-steel transition of manganese can be doubled. This makes it possible to cut twice the wastes associated with manganese ore extraction without affecting steel output.

The by-products of the nitrate method — i.e. calcium nitrates and nitrates of other elements contained in the ore, — are in constant demand on domestic and global markets.

The waste products include neutralized ore slime, which mainly contains silica. It also contains a small amount of manganese, which comes in an insoluble form.

In terms of the chemical process, a higher-grade ore improves the process performance by reducing the material flows at leaching and washing stages and by producing less slime [13–15]. For evaluation purposes, we shall suppose that the above advantages help save 50 rubles per ton-percent during the chemical treatment stage. So, if, due to the beneficiation process at a concentrator plant that is close to the deposit, the manganese concentration in the ore goes 1% up within the given price rise range, such beneficiation process would prove feasible. The grinding operation used to reach the required dispersity can be combined with beneficiation. The best option would be to use finer material resultant from the ore concentration at a large-scale site, which would also have been subjected to magnetic separation [15–18]. It is important that the nitrate method works better for finer material, which is of no interest to metallurgical industry.

Bottom ferromanganese concretions and waste products generated by manganese industry provide good materials for the nitrate method. Ferromanganese concretions shall be considered further on as a type of oxide ores, and for their treatment a few special processes will be employed additionally as part of the nitrate method. Additional process stages will also have to be employed when processing metallurgical slags and other manganese containing wastes.



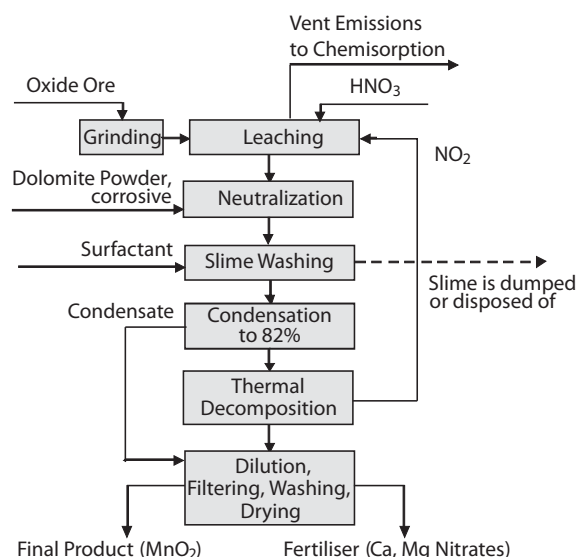


Fig. 3. Block diagram: nitrate method for oxide ore

The composition of the primary material and its characteristics can have a tremendous effect on the process economics. The composition of the primary material can influence the slime characteristics, as well as the amount and composition of the by-product, i.e. calcium-magnesium nitrates. In certain instances, up to 1 ton of fertilizers can be produced per ton of SPYR.

The key characteristic of the primary material is the recoverability of manganese. Multiple experiments show that the use of nitrates delivers the most efficient breakdown process as calcium and magnesium make a quick transition to a solution, whereas the use of sulfuric acid, for example, would result in the formation of poorly soluble gypsum, which would impede further leaching of manganese.

It was established that, for the majority of oxide ores with excessive amounts of nitrogen oxides, the leaching process takes minutes at 50 °C and, what is crucial, no frothing occurs. During a continuous process when the final concentration of the solution reaches 25% and a certain leaching rate needs to be maintained, the Mn recovery reaches 90% in 20–30 minutes. The Mn recovery rate can be taken to 94% and higher by raising the acid-

ity of slurry (which leads to an increased consumption of the neutralizing reagent), raising the pressure to 2–3 atmospheres or extending the leaching time. However, the optimum process corresponds to  $92\% \pm 0.5\%$ .

Fig. 3 shows a nitrate method diagram.

1. Storage area for samples of manganese oxide and manganese carbonate ores and ferromanganese concretions, container with nitric acid.

2. Reactor area houses an electric manganese nitrate thermal decomposition reactor (TDR) and a nitric acid leach reactor (NLR) for manganese ore.

3. Nutsche filter;

4. SPYR drying and packaging area;

5. Nitrous gas absorbers;

6. Slime pit.

### Primary Ore, Ingredients and Products

**Manganese ore.** Manganese oxide and manganese carbonate ores from Russian deposits, samples of ferromanganese concretions of any compositions after physical and mechanical preparation in the first section. Required concentration:  $35\% < \text{Mn} < 7\%$ , size: 2 mm.

Nitric acid  $\text{HNO}_3$  (GOST 701-89). Molecular weight — 98.08; boiling point = 330 °C; density at 20 °C — 1.839 kg/m<sup>3</sup> at 80% and — 1.200 kg/m<sup>3</sup> at 23%; melting point = 8.48 °C; MPC = 1 mg/m<sup>3</sup> (hazard class 2). Moderately hazardous substance, strong oxidizer. It may irritate upper airways. When in contact with skin, it may cause a strong burning pain and actual burns. Hazard class 3.

**Products.** Synthetic pyrolusite. Formula:  $\text{MnO}_2$ ; crystalline modification:  $\beta$ . Silver powder, insoluble in water. Dispersity: 90% in the range of 50–100  $\mu\text{m}$ . Bulk weight — 2.5 g/cm<sup>3</sup>. Not flammable or explosive. Hazard class 2. MPC in workplace air = 0.3 mg/m<sup>3</sup>.

**By-products** — Calcium-magnesium nitrates; Application: agricultural and other industries. Ore slimes: Application in construction industry.

### Process Implementation

The SPYR production process can be described with the following reaction:



The reaction takes place in the calcium and magnesium nitrate medium at  $T = 180$  °C and at atmospheric pressure. 25% manganese, calcium and magnesium nitrate solutions are used to launch the process. Further on process solutions are used that are generated during leaching and absorption stages.

The TDR is manually filled with 100 kg (83 l) of starting nitrate solutions. Such solution contains 12.5% of Mn nitrate and 12.5% Ca and Mg nitrates. The weight ratio between Mn nitrate and Ca and Mg nitrates should be 1/1 (Fig. 4). An electric heater comes on. Water evap-

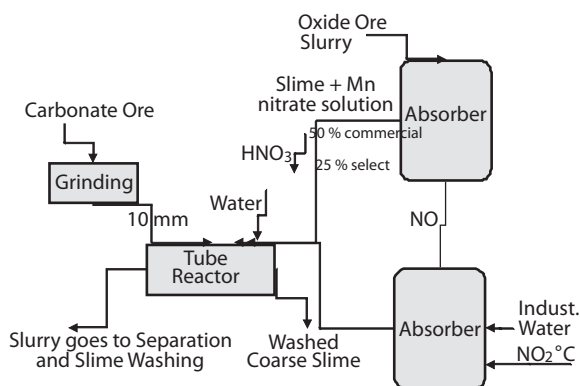


Fig. 4. Block diagram: nitrate method for carbonate ore

oration is the only process that takes place in the reactor before the temperature has reached 150 °C. Thermal decomposition occurs when the salt concentration goes above 60% and the temperature exceeds 160 °C. The resultant nitrous gases diluted with water vapours arrive in the NLR.

Slurry composition after leaching:

Solid phase: 7–8 kg — tailings.

Liquid phase: 12 kg (12%) — Mn nitrate; 3 kg (3%) — Ca and Mg nitrates; 85 kg (85%) — water.

15 kg of ore (equivalent to the same amount of 25% manganese ore) are loaded in the NLR. Then 15 l of water are added so that the starting solid-to-liquid ratio was 1/1. Due to evaporation in the TDR, the final solid-to-liquid ratio is 1/12. There is an expansion tank between the two reactors designed to stop the ore slurry from migrating from the NLR to the TDR.

Slurry composition after thermal decomposition:

Liquid phase: 1.25 kg (7.2%) — Mn nitrate; 12.5 kg (73%) — Ca and Mg nitrates; 6.0 kg (20%) — water.

Gaseous phase: 6.4 kg — nitrogen oxides; 70.0 kg — steam.

Solid phase: 5.5 kg —  $\text{MnO}_2$  (SPYR).

Before being drained, the slurry is diluted with 40 liters of water for the total concentration of salts in the liquid phase to be 30%. Composition of the diluted slurry: 46 l — water; 5.5 kg — SPYR. Due to condensation and the exothermicity of the leaching reaction, the temperature in the NLR rises to 50–100 °C. For the type of reactor used, the degree of nitrous gas absorption in the NLR, according to the mass exchange, should not exceed 97%.

About 5% of unabsorbed gases, which mainly include nitrogen oxides (NO), go to the absorbers. The absorbers have extended surface packings and are filled with finely dispersed manganese dioxide slurry with the liquid-to-solid ratio = 3/1, 20 l in each absorber.

Just one of the absorbers is used for accurate analysis of the nitrogen oxide absorption environment. The absorber is equipped with entry and exit rotameters, an electric belt heater and an indicating thermometer. The composition and temperature of the liquid and solid parts of the slurry in the absorber are varied to find optimum conditions for nitrogen oxide absorption. The nitrogen oxide flow rate at the exit from the NLR may be 10% of the total nitrogen oxide flow rate at the exit from the TDR, i.e. 10 l/min. If the exit flow rate is too high, the reactor will need to be shut down and the temperature normalized. Only after that the solutions can be discharged to the Nutsche filter.

The slurry is drained from the reactors in polyethylene tanks, neutralized with dolomite powder, soda or ammonia to the pH level = 4.0, and sent to the Nutsche filter for filtering and washing. The filtrate, which contains manganese, calcium and magnesium nitrates, is put back in the TDR. Slime in the amount of 1.5–2.0 kg per 1 kg of final product goes to an industrial slime washing system and is used to analyze possible disposal techniques.

The material in the TDR is diluted to reach 30% of the total salt concentration in the liquid phase and is dumped in a polyethylene tank. The slurry is decanted in the tank, the condensed part is filtered by the Nutsche filter, washed with a small amount of water and dried to a 5% humidity level. The liquid part is collected in one of the containers and sent to the TDR as an inert medium. Excess calcium and magnesium nitrates are separated for further processing to become fertilizers or deicing chemicals.

All the units operate with a slight excess pressure equal to the absorber resistance, which does not exceed 1.5 m  $\text{H}_2\text{O}$ . It means that the gauge pressure  $P_{\text{exc.}} = 0.15$ – $1.15$  atm ( $P_{\text{abs.}} = P_{\text{exc.}} + P_{\text{atm}}$ ). There are three instrumentation units that are used. ORCOM — D49 is used in an on-off mode to control the temperature in the TDR.

There are units for nitric acid regeneration and nitrous gas utilization. 25–30% nitric acid can well be used in ore leaching. Besides, it is nitrogen oxides that the oxide ore slurry can absorb so well under certain conditions. This helps achieve their complete recovery and, thus, tackles one of the biggest challenges faced by nitrogen industry.

### Electrolysis Line

Two electrolytic processes are implemented to produce electrolytic manganese dioxides (EMD) and manganese metal from manganese sulfate solutions. The equipment includes two electrolytic baths of relatively small sizes.

The electrolytic processes are designed to produce electrolytic manganese dioxides (EMD) [19] and electrolytic manganese metal (EMM).

The rated capacity of the electrolytic manganese dioxide (EMD) line is 10 kg/year, and it is 10 kg/year for the electrolytic manganese metal (EMM) line.

The main process equipment is made of copolymer with a polypropylene base, whereas the high-temperature cells are made of homopolymer which can withstand temperatures up to 1,000 °C. To prevent evaporation and reduce aerosol losses, the equipment is fitted with special covers with filters.

The EMD and EMM lines comprise the following components:

EMD cell with a cover and heaters.

EMM cell with a temperature control system.

Accumulation tank for the  $\text{MnSO}_4$  solution.

Sulfide cleaning reactor for manganese sulfate solution.

Cartridge filter.

Accumulation tank for purified  $\text{MnSO}_4$  solution with a decantation system.

Process solution and additive preparation unit.

A set of tanks for EMD and EMM washing and conditioning.

The process tanks are interconnected with polypropylene lines, which have regulators and supply valves. The lines consist of sections, so the process flow can be quickly redirected.

## Conclusions

The authors developed a hydrometallurgical complex to process low-grade manganese ores into high-quality products. Concentrates produced through hydrometallurgical processes can be processed to produce manganese metal and low-carbon ferroalloys.

A leaching process was developed for manganese ore samples with manganese sulfate and manganese nitrate solutions as final products;

A technique was developed to produce electrolytic manganese dioxides, electrolytic manganese metal and a chemisorption manganese oxide complex from manganese sulfate solutions.

A technique was developed for obtaining synthetic pyrolusite from nitrate solutions. Synthetic pyrolusite is a pure  $\beta$ - $\text{MnO}_2$ , which can serve as primary material in pyrometallurgical and chemical industries. It should be noted that a certain amount of nitric acid is reproduced in the process.

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