

**CONTRACT FOR NON-CONSULTING SERVICES**

**Processing of Manganese Oxide Materials**

**GE-GITA-208861-NC-DIR**

**Final Report**

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შეამოწმა და დასტურდა  
ნაშრომის შედეგები:  
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### **General Information about the Project**

**Project title:** Processing of Manganese Oxide Materials

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#### **Beneficiary organization:**

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## SUMMARY

The research group (supervisor G. Tsursumia) from the Ivane Javakishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry developed novel electrometallurgical technology and using this technology processed reduced and nonreduced manganese ores supplied by the Manganese Metal Company LLC (MMC) from Republic of South Africa to produce high purity ( $\geq 99\%$ ) manganese sulfate monohydrate (HPMSM).

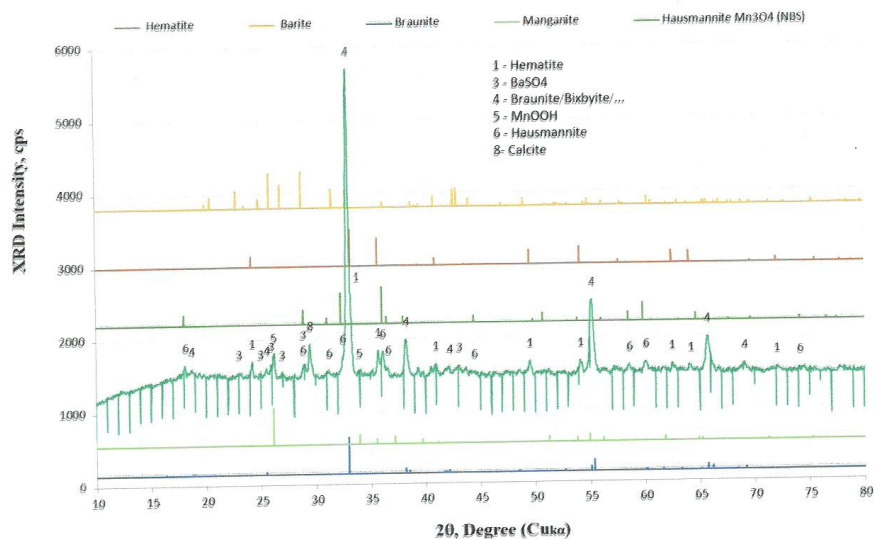
It was found that:

- Mineralogical composition of South African oxide ores significantly differs from those mined in Chiatura region of Georgia. While pyrolusite ( $\beta\text{-MnO}_2$ ) is the main mineral containing manganese in Georgian manganese ores, South African manganese ores (nonreduced ores) do not contain pyrolusite and main manganese containing minerals are braunite-bixbyite. There are also in lesser amount hematite, barite, manganite, hausmannite and calcite. Reduced ores from South Africa mainly contains manganosite, lesser amount of barite, andradite, calcite, magnetite and very small amount of braunite.
- Due to different mineralogical content, processing of South African oxide ores (nonreduced) using electro-leaching proceeds with relatively low extraction efficiency (60-70%) of manganese, whereas the same parameter in case of Georgian oxide ores is 98%. For the enhancement of manganese extraction efficiency, South African oxide ores can be processed in the autoclave under high temperature (100-120 °C). This approach can be considered as alternative of high temperature (850 – 900 °C) reduction process.
- South African oxide ores were electro-leached using  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox system and reduced ores were leached by sulfuric acid to obtain solution of manganese sulfate solutions.
- Hydrolysis was applied to remove iron impurities from the sulfate solution. Sulfide purification was exploited for purification from heavy metals.
- In several experiments, manganese fluoride ( $\text{MnF}_2$ ) was added to remove calcium and magnesium impurities. Addition of fluoride created some excess of fluoride ions which caused the corrosion of inner walls of autoclave. Due to lack of time we could not fulfil our plan to supply dosed fluoride ions via anionite to solution and remove calcium and magnesium as their fluoride salts by help of mobile fluoride ion. After fluoride purification, fluoride ions were found in crystals of manganese sulfate monohydrate salt obtained by autoclaving.
- Multiple recrystallizations of manganese sulfate monohydrate salt in autoclave (i.e. redissolving of crystalized salt in DI water and autoclave recrystallization) were performed to decrease the amount of impurities of calcium, magnesium, sodium and potassium in the solution of manganese sulfate;
- After 3-4time recrystallization of manganese sulfate monohydrate, the salt was treated in pure methanol to farther reduce amount of impurities. Impurities were reduced in the target product but technical conditions of used autoclave (corroded inner walls) did not allow change the acidity of manganese sulfate solution in order to farther reduce amount of impurities in the salt.
- Expenditure ratios of complete technological cycle are given for apparatus and reactors based on conducted research.
- Defined amounts of manganese sulfate monohydrate salt are obtained based on conducted technological processes.

**1. Data of different technological stages for production of high purity ( $\geq 90.0\%$ ), 3 kg (electro-leaching) and 5 kg (sulfuric acid leaching) manganese sulfate monohydrate (HPMSM) from concentrated solutions of manganese sulfate monohydrate obtained using autoclave processing and farther purification**

1.1. To find out the reason of low efficiency extraction (around 70%) of South African manganese containing oxide ores (not reduced) performed by electro-leaching, samples of nonreduced, reduced and sludge left after electro-leaching were studied by X-ray phase analysis. The research was conducted using X-ray diffractometer ДРОН-4.07 under conditions: БСВ-28 tube with copper anode;  $\text{Cu}_{K\alpha}$  radiation filtrated by nickel foil ( $\lambda=1,54184\text{\AA}$ ); tube voltage – 40kV; tube current – 20mA.

On the X-ray diffractogram of nonreduced ore, mostly peaks of braunite-bixbyite mineral group are identified. Lesser intensive X-ray diffraction peaks appeared for hematite, barite, manganite, hausmannite and calcite. Based on a weak X-ray diffraction peak at  $2\theta=25.5^\circ$ , we can assume that the sample contains relatively high amount of braunite (figure 1 and 2).



**Figure 1.** X-ray diffractogram: nonreduced ore. ( $\text{Cu}_{K\alpha}$ -1gr/min)

Mostly manganosite diffraction peaks are appeared on X-ray diffractogram for reduced ore. Relatively low intensity is seen for barite, andradite, calcite, manganite and most likely very small amount of braunite.

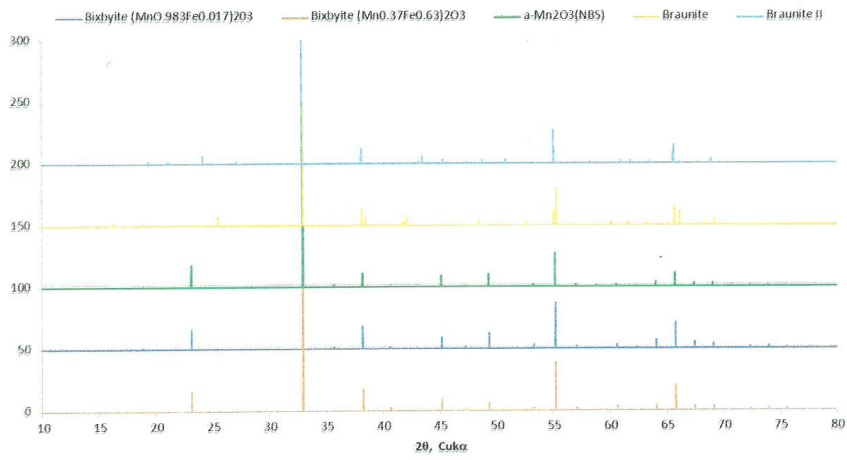


Figure 2. Braunite-bixbyite mineral group X-ray hatch diffractograms

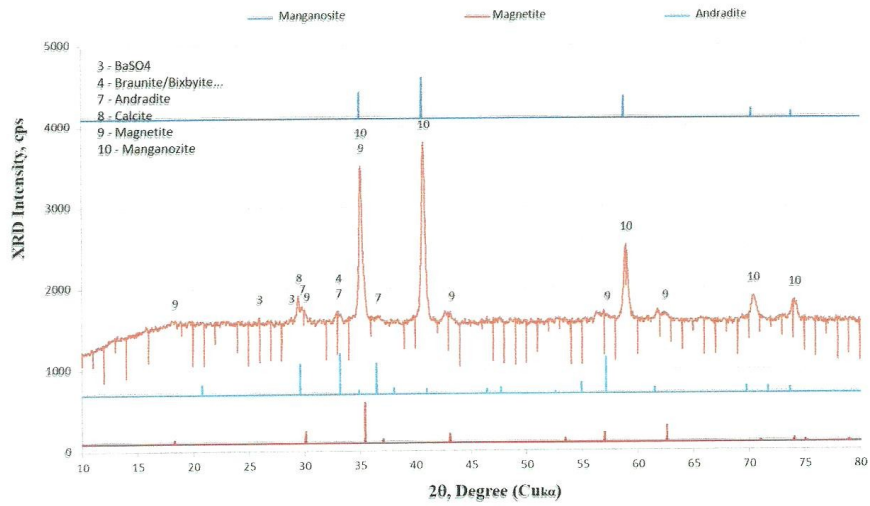


Figure 3. X-ray diffractogram: reduced ore (Cuka-1gr/min)

On an X-ray diffractogram of sludge left after electro-leaching (figure 4), highly intensive diffraction peaks of  $\gamma$ -CaSO<sub>4</sub> or/and CaSO<sub>4</sub>·0.625H<sub>2</sub>O appeared ( $\gamma$ -CaSO<sub>4</sub> or/and CaSO<sub>4</sub>·0.625H<sub>2</sub>O show nearly identical diffractograms). These peaks interfere with other phases, especially with manganite and therefore these

samples were additionally treated with water to remove  $\text{CaSO}_4$ . Peaks of braunite, hematite, barite and andradite appeared on X-ray diffractogram for the washed sample (figure 5).

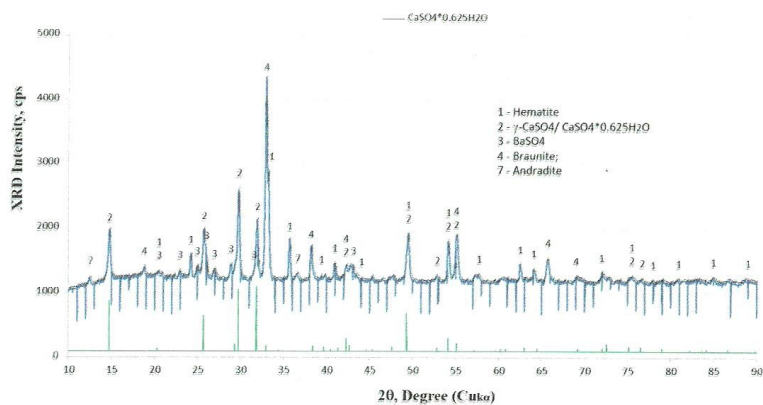


Figure 4. Diffractogram: Sludge obtained after electro-leaching (Cuka-1 gr/min)

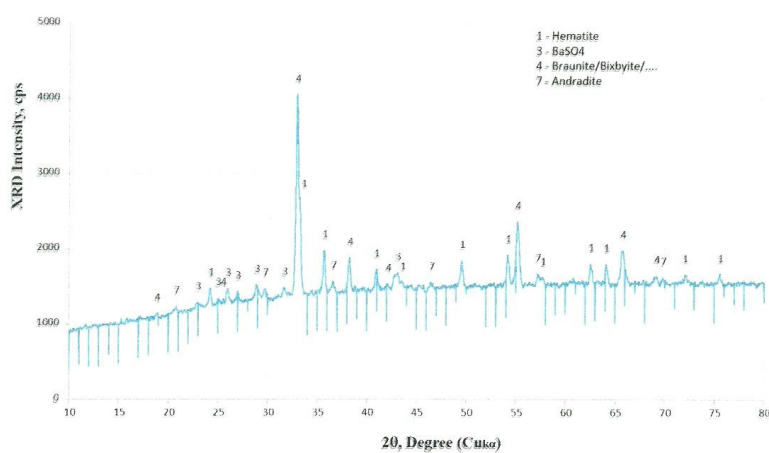
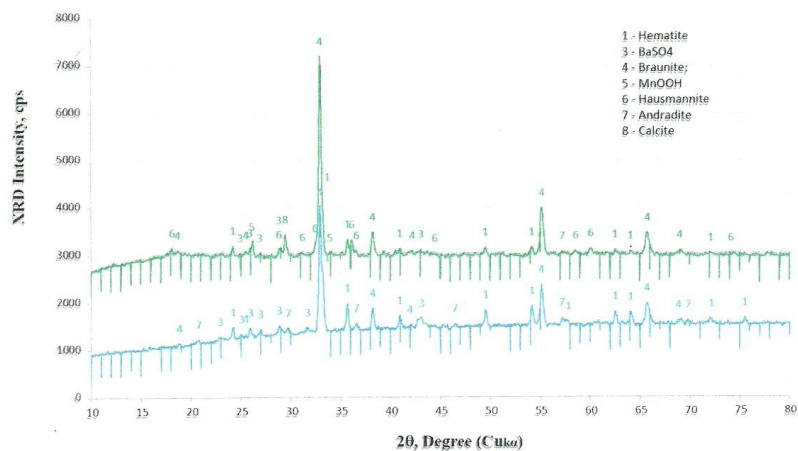


Figure 5. Diffractogram: Washed sludge obtained after electro-leaching (Cuka-1 gr/min)

Based on comparison of diffractograms of initial nonreduced ore and sludge one can conclude that under effect of  $\text{Fe}^{2+}$  manganite and hausmanite and leaching of braunite-bixbyite group minerals is complicated (especially braunite).



**Figure 6.** Diffractograms: Nonreduced ore (Cuk $\alpha$ -1gr/min) \_\_\_\_\_  
Sludge after electro-leaching (Cuk $\alpha$ -1gr/min) \_\_\_\_\_

Therefore mineral braunitz should be the reason of incomplete extraction of manganese from South African nonreduced oxide ore treated by electro-leaching.

To increase efficiency of leaching, relatively high temperature (60-70 $^{\circ}$ C) electro-leaching was conducted. Under this conditions extraction of manganese was increased by 10%. Application of higher temperature will require exploitation of autoclave. We recommend electro-leaching of South African to be done in the autoclave at high (100-120 $^{\circ}$ C) temperature. This approach can be considered as an alternative of high temperature reduction of oxide ore.

Applying electro-leaching, 92-95g/l Mn $^{2+}$  containing solution was prepared and subsequently purified from ions of iron by hydrolysis and from heavy metals by sulfide purification. Conditions of electro-leaching are: 20A, voltage 3.0V; 12.6 L of H $_2$ SO $_4$  + 3-5g/L Fe $^{3+}$ , pH 1, 1 kg ore (44% Mn); obtained suspension circulates in electrochemical reactor; temperature 25-28  $^{\circ}$ C; 250Ah electricity is needed to prepare 20g/L Mn $^{2+}$  solution. After autoclave processing of purified solution crystals of manganese sulfate monohydrate was obtained. Purification of solution, autoclaving and farther treatment of obtained salt crystals was done in analogy of treatment of solutions obtained after leaching of reduced oxide ores. Technological parameters of purification and autoclave treatment of solutions obtained after leaching of reduced oxide ores and purification of obtained salt are given below in details.

### **1.2. Technological parameters of leaching of reduced oxide ores**

Equipment for production of manganese sulfate solution of high concentration from South African reduced oxide ore is described in the previous report. Leaching was conducted under simultaneous supply of concentrated sulfuric acid (95% H $_2$ SO $_4$ ) and milled ore at 70 $^{\circ}$ C and pH 1, under 300-350rpm conditions. Starting amount of ore was 10kg (47 % Mn). Manganese extraction efficiency - 95%.

### **1.3. Technological parameters for hydrolysis purification of iron ions (Fe $^{3+}$ )**

Concentration of Fe<sup>3+</sup> in the solution reached 8-9g/L. To remove Fe ions, the solution of manganese sulfate was heated to 92-93°C, pH was decreased to 5 by adding ammonia and after half an hour intensive stirring was hot filtrated through the paper or nutsche filter lavsan cloth.

### **1.5. Technological parameters of sulfide purification of heavy metals**

After purification from Fe<sup>3+</sup> ions, solutions are being purified from impurities of heavy metals (Ni<sup>2+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) using sulfide purification. As a purifying agent, solution of ammonium sulfide obtained by passing hydrogen sulfide through ammonia until complete saturation, was used. Sulfide purification was done for one hour at 70 °C and pH 6.5 -7 and under intensive stirring. Sulfide purification needs to be performed several times until pink color manganese sulfide is produced. After filtration, pH 2 sulfuric acid was added and solution was boiled to remove colloidal sulfur. After purification the solution was ready for the autoclaving.

### **1.6. Technological parameters of purification of manganese sulfate solution from calcium and magnesium ions.**

Due to requirements for quality of manganese sulfate salt, presence of calcium and magnesium ions in MSM is not desirable. The amount of these ions should not exceed 100ppm [Chemical industry standard HG/T 4823-2015, CHINA].

Widely spread method of elimination of calcium and magnesium ions from solutions of manganese sulfate is addition of manganese fluoride (MnF<sub>2</sub>) which makes deposition of calcium and magnesium fluorides. This approach must be carefully controlled since there is a risk of contamination of manganese sulfate salt crystals with fluoride ions. In our case, fluoride purification caused corrosion of inner surface of autoclave. Due to this complication, crystallization of salt from these solutions was done by evaporation.

Table 1.

Analysis of manganese sulfate monohydrate salt crystallized by evaporation of solutions purified fluoride purification																
	Mn%	Fe	Ca	Mg	Na	K	Ni	Co	Al	Cu	Ba	B	Cr	Zn	F	Moisture, %
Analysis is done in Rustavi	32.3		150	206	25		<1	<1	<1	<1						0.069
Analysis is done in South Africa	32	~43	144	248	44	23	<3	<2	<7	<0.1	2	8	9	2	241	
Analysis is done in Rustavi	31.9	1.09	110.3	53.9	17.58	2.52	0	0.1	0.7	0	0.22					0.195
Analysis is done in South Africa	32.3	<5	~61	~46	96	35	<1	<1	<11	<0.1	4	10	6	6	2500	

Due to lack of time we could not fulfil our plan to supply dosed fluoride ions via anionite to solution and remove calcium and magnesium as their fluoride salts by help of mobile fluoride ion.

To remove calcium, magnesium, sodium and potassium impurities we applied widely spread multiple crystallization method which was performed in the autoclave i.e. crystallized salt was redissolved in DI water, acidification to pH 2 and repetitive recrystallization from the autoclave. This operation was done 3-



4 times. To protect inner, working surface of autoclave from corrosion it was covered with silicon, Akfix HT300, stable at heating up to 300 °C which was mixed with powder of fluoroplast served as a filler.

2.9 L of purified solution with concentration of 94-110 g/l  $Mn^{2+}$  was placed in 3.0L volume autoclave (China, GSH-3L magnetic seal reactor) with filtration device. Autoclaving was performed at 165 °C, 6-6.5 atm pressure and 50-60rpm stirring. After achieving this condition the lower valve of the autoclave was opened and under the pressure 2.0 L of mother solution with 18 g/L content of manganese was delivered through the filter. After opening the autoclave, the salt was taken and dried in the oven under 100 °C for 4 hours. The dried salt was milled in agate miller and sieved through the sieve with cell size 0.4mm. After this procedure the salt was washed in the pure methanol (99.9%). The average composition samples of crystalized salt is given in the table 2.

Table 2

Origin	Mn	Fe	Ca	Mg	K	Cu	Co	Na	The amount of sample left
	%	ppm							
The salt obtained by autoclave crystallization of solutions (Mn 100-110 g/l, Ca 400-700 mg/l, Mg 400-500 mg/l) obtained after leaching of manganese containing material, hydrolysis and sulphide purification	25.45	9	2139	521	110	0.4	0.5	204	
	26.14	8	2036	674	111	0.5	0.4	254	
	25.52	8	2194	573	102	0.4	0.1	244	
	25.47	8	2303	537	61	0.4	0.2	238	
	25.11	8	2352	513	64	0.5	0.2	270	
	25.16	7	2303	514	56	0.4	0.3	246	
Averaged sample washed in methanol from 8 kg of salt of the first crystallization.	28.71	10.6	2063	118	81	0.3	0.7		120
Averaged sample from 5kg salt of the second crystallization	29.51	15.8	1620	129	41.1	0.3	4.5		124
Salt of the second crystallization washed in methanol	30.28	13	1548	128	50.8	0.3	4.3		660
Averaged sample from 3kg salt of the third crystallization	31.9	15.2	457	166		0.3	4.7		510
Salt of the third crystallization washed in methanol	32.05	14.1	376	144		0.3	4.1		750
Averaged sample from 0.9 kg salt of the fourth crystallization	32.2	19.1	375	310		0.4	4.7		50
Salt of the fourth crystallization washed in methanol	32.46	17.3	190	130		0.4	4.5		463
The salt obtained by autoclave crystallization of solutions obtained after leaching of manganese containing material, hydrolysis, sulphide and fluoride purification	32.52	50.7	375	316		0.3	4.5		150

The results show that amounts of calcium, magnesium sodium and potassium after recrystallization were significantly lowered. The existence of heavy metals in the sample is the result of corrosion of inner walls of autoclave.

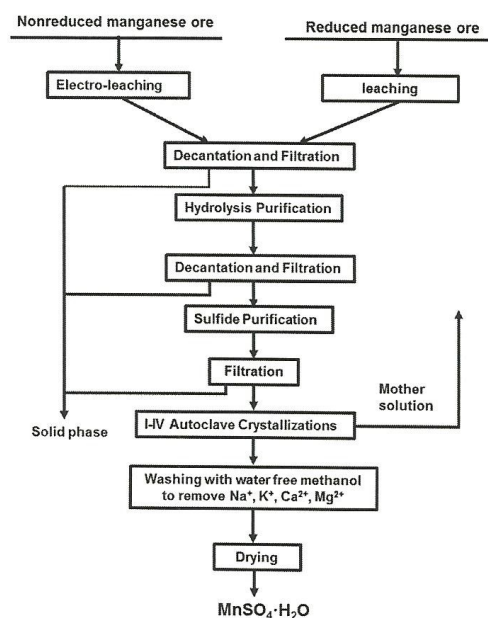
#### **1.7. The method of washing manganese sulfate monohydrate salt in pure methanol**

Pure (99.9%) methanol was used to extract impurities from the powder of manganese sulfate salt. The extraction was done in 2.0 L, 3-neck round bottom flask equipped with anchor type polypropylene stirrer,

reflux condenser and a thermometer. The flask was heated up using a hot plate. For extraction, 100 g of salt was placed in 250 mL methanol. Suspension was treated at 38-40 °C and under intensive stirring for 0.5 hours. Next, suspension was filtrated under vacuum using #3 Buchner funnel. Washed salt was placed on glass tray and dried in the oven at 100 °C for 4 hours.

### **1.8. Monitoring of various stages of technology of treatment of manganese ores**

For obtaining high quality manganese salt it is necessary to monitor each stage of treatment of manganese ores. In solution, besides the control of main component – concentration of manganese ions, it is important to monitor impurities after each technological stage. This control was performed in the company “MN Chemical Georgia” (Rustavi) analytical laboratory according Chinese standard - HG/T 4823-2015 - Manganese sulfate for battery materials using ICP (contract N180/06 06.04.2021). Figure 7 shows the main technological scheme, according which the treatment of manganese containing materials.



**Figure 7.** Technological scheme for treatment of manganese containing oxide materials

## 2. The main material and energy costs of technological cycle for production of high purity manganese sulfate monohydrate (HPMSM)

The main material and energy consumption of technological cycle is calculated considering parameters of our apparatus and equipment.

### 1. The expenditure of consumption manganese containing oxide material

- In initial material content of manganese, mass % Mn: in nonreduced ore: 44.1; in reduced ore – 47%.
- Extraction efficiency from nonreduced ore treated by electro-leaching is 66%.
- Extraction efficiency from reduced ore is 95%.
- The loss of manganese at stage of hydrolysis purification of solution is 5%.
- The loss of manganese at stage of sulfide purification of solution is 3.2%.
- The loss of manganese at stage of decantation and filtration is 1.2%.
- The loss of manganese at stage of filtration after sulfide purification of solution is 0.6%.
- The loss of manganese after mother solution exiting the autoclave is 14%.
- The loss of manganese after washing the salt with methanol is 1%.

According listed reasons extraction of manganese per target product ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  99.9%) is 32.3% from nonreduced ore and 46.5% from reduced ore.

The consumption of manganese containing oxide material per target product is 2.3 kg/kg for nonreduced ore and 1.5 kg/kg for reduced ore.

### 2. The consumption of sulfuric acid

- The concentration of sulfuric acid - 95%
- Consumption of sulfuric acid with regard to manganese and all soluble in sulfuric acid impurities
- Consumption of sulfuric acid after various stages of purification of solutions obtained after leaching.

Based on listed reasons the total consumption of sulfuric acid per target product is 1.3 kg/kg

### 3. Consumption of Methanol

- The loss of methanol after purification (99%) is 2%
- The loss of methanol during treatment of salt is 2 %
- The loss of methanol during regeneration (refluxing) is 16%

The total consumption of methanol in regards to final product is 3.1L/kg

### 4. Consumption of Ammonia

1.5L of 22 % concentration ammonia is consumed during treatment of 100g/L Mn, 40 L solution. Consumption of ammonia considering production of target product is 0.052 kg/kg.

### 5. Consumption of sodium sulfide

Considering existence of heavy metals and extraction efficiency of manganese, consumption of sodium sulfide for production of  $(\text{NH}_4)_2\text{S}$  from  $\text{Na}_2\text{S}$  (60%) with conversion degree of (90%) is:

In case of nonreduced ore – 0.3kg/kg

In case of reduced ore – 0.2kg/kg

### 6. Consumption of electrical energy

Considering main parameters during electrolysis (volume of reactor 12.6 L, load 20 A, voltage 3 V, 125 hours which is time needed to accumulate 20g/L manganese) is 2.08 kWh/kg

In the reactor with a stirrer (power – 0.5 kW, ore supply 800g/h), considering the process of leaching of reduced ore and production of target product, consumption of electrical energy is 0.93kWh/kg.

Considering parameters of the autoclave during the process of crystallization (heater – 4kW, stirrer – 1 kW, rotation of a stirrer – 1.5 h, the time of autoclaving – 2h, efficiency – 900g), consumption is 10.55 kWh/kg  
Total consumption of electrical energy during technological cycle considering manganese containing material is given in the table 3.

Table 3.

Consumption of electrical energy during treatment of manganese containing material, kWh/kg		
Process	Nonreduced ore	Reduced ore
Electro-leaching	2.08	
Leaching in the reactor with a stirrer		0.93
Crystallization of salt	10.55	10.55
Total	12.63	11.48
Other processes	1.26	1.15
Total consumption	26.52	24.11