THE MEANS OF PRODUCTION OF POTASSIUM PERMANGANATE THROUGH CALCIUM PERMANGANATE

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Permanganate is produced from the existing lean ores for which the cheap carbonate ores are used and which are not of the deficit in the Russian Federation. A lot of studies were taken and was chosen the liquid phase process with using the gaseous chlorine as an oxidant. To maintain the neutral pH the carbonate ore contains carbonate of calcium, which acts as a buffer in the liquid phase chlorination of the carbonate ore. At 400-800C temperature the ideal conditions are made for chlorine hydrolysis with producing the hydrochloric acid (HCl) and hypochlorous acid (HOSl). The weak hydrochloric acid reacts with the calcium carbonate ($CaCO_3$), and in these conditions HOSl oxidizes manganese oxide IV (MnO_2) to $Ca(MnO_4)_2$. The liberated CO_2 promotes the oxidation of the unstable manganese salt due to the other with direct production of $Ca(MnO_4)_2$ and MnO_2.

Keywords: dioxide of manganese; chlorine; potassium permanganate; calcium carbonate

Potassium permanganate has a reasonable industrial significance. Its facilitation is based upon oxidation characteristics; $KMnO_4$ is used as a rective for permanganatometry, revealing dual links, synthesising glycols, oxides, aldehydes and ketones, saccharin. Potassium permanganate is also used for bleaching variuos materials, in processes of synthesising and analysing organic substances, colorants. It is known that it is facilitatated as an indicator of polymerization, in production of catalysts, air cleaning, pyrotechnics, antiseptic medications, oxidising «caps» of nanotubes [1–2].

Historically the first method of receiving potassium permangant [3] is synthesising potassium manganate (VI) from polianite and alkali in reaction with oxygen and baking on the air:

$$2MnO_2 + O_2 + 4KOH = 2K_2MnO_4 + 2H_2O. \tag{1}$$
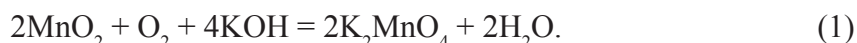
Then the received alloy is lixiviated with water, and transformation of manganate into permanganate takes place in the received alkali solution. Stage of transforming manganate into permanganate can include:

1. Boiling the solution – formation of potassium permanganate takes place as a result of disproportioning manganate (VI) according to equation of reaction:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH. \tag{2}$$

2. While processing CO_2 solution the process of disproportioning accelerates, the reaction takes place according to equation:

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3. \tag{3}$$

Due to formation of MnO_2 the process is unfavourable and it is necessary to regenerate KOH from the formed potash according to the reaction:

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3\downarrow. \tag{4}$$
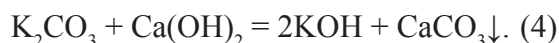
3. Oxidation of manganate with chlorine according to reaction:

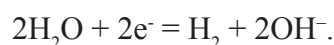$$2K_2MnO_4 + Cl_2 = 2KMnO_4 + 2KCl \tag{5}$$

is also unfavourable due to losses in potassium as KCl, regenerating KOH form them via electrolysis requires a lot of resources. Therefore, electromechanical method of transforming manganate into permanganate is being developed.

Nowadays a technology of receiving potassium permanganate through a combined (two-stage) method is generally accepted [4]. Polianite is mixed with KOH abd exposed to alloying in baking pots at the first stage, the reaction takes place according to equation (1).

The received allow is lixiviated, and the received solution is exposed to electrolysis at the second stage. At the same time, ion MnO_4^- is oxidized on anode:

$$MnO_4^{2-} - e^- = MnO_4^- \tag{6}$$

and alkali and hydrogen are formed on katode:

$$2H_2O + 2e^- = H_2 + 2OH^-.$$

Final equation:

$$2K_2MnO_4 + 2H_2O = 2KMnO_4 + 2KOH + H_2. \tag{7}$$

Crystals $KMnO_4$, formed on electrolytic cell, are discharged, washed, and exposed to re-crystallization, and then dried and packed [3].

The described combined technology of receiving potassium permanganate has the following disadvantages: long duration of alkaline alloying, low output of potassium manganite, high energetic costs. Therefore, works on improving production process have been undergoing constantly, their objective is to decrease energy costs and increase product output.

One-stage technology of receiving potassium permanganate from manganese dioxide has been suggested by an author of American patent [5]. This technology consists of electromechanical oxidation of MnO_2 suspension in solution of potassium hydroxide with implementation of katode in porous container and high concentration of alkali ($10–25$ mole/dm^3) inside the container. The method has been suggested for regenerating permanaganate in alloying baths and is described by a great consumption of electric energy (14 kVt·hr/kg) that exceeds energy consumption ($0,7$ kVt·hr/kg) of the combined technology. The listed methods testify for a continuous search in the studied area that is linked to developing methods that provide for a complete facilitation of raw material (transforming a greater part of initial materials into the product) and increase in product output.

Dozens of patents are known. One-stage tehcnologies are being developed. However, only one method is used in industry – electromechnical oxidation of potassium manganate (IV).

Disadvantages of the existing method of receving potassium permanganate:

1. Long duration of the process of alkaline manganate alloying. This stae continues for no less than 24 hours.

2. Insufficient output of potassium manganate (VI) suring the stage of alloying – no more than 60%, and, therefore, greater consumption of raw materials.

3. The process of producing KMnO4 includes many operations with a powerful alkaline solution.

4. Potash is formed in case of continuous contact with air, and therefore, a necessity to regenerate alkali emerges. During caustification of potash with quicklime – CaO or slaked lime – $Ca(OH)_2$, consumption equals $0,7$ t (in calculation to 100% of CaO) per ton of permanganate.

5. High specific consumption of energy – 1383 kJoule/mole of permanganate. Therefore, development of methods that possess improved characteristics is reasonable [1].

The objective of this work is to receive permanganates of the existing impoverished ores, cheap carbonate ores that are commonly present in Russia, have been used for this purpose. As a result of numerous exams, we have defined liquid-phase process with facilitation of gaseous chlorus as an oxidant. In order to maintain nearly neutral pH of the solution, carbonate ore contains calcium carbonate that serves the purpose of buffer during liquid-phase chlorination of carbonate ore. Perfect conditions for chlorus hysrolysis with receipt of HCl and HOCl are created under temperature $40–80\,°C$. A weak hydrochloric acid interacts with $CaCO_3$, and HOCl oxidates MnO_2 to $Ca(MnO_4)_2$ in these conditions. The discharged CO_2 provides of oxidation of one unstable manganese salt by another with a direct receipt of $Ca(MnO_4)_2$ and MnO_2.
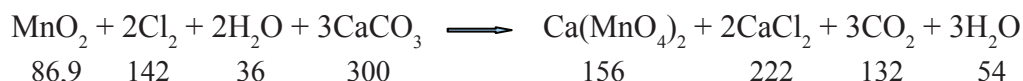
Chemism of the process is represented as:

$$MnO_2 + 2Cl_2 + 2H_2O + 3CaCO_3 \longrightarrow Ca(MnO_4)_2 + 2CaCl_2 + 3CO_2 + 3H_2O$$

| $86,9$ | 142 | 36 | 300 | 156 | 222 | 132 | 54 |

Table 1

Composition of manganese ore

Composition of manganese ore	Mass, g	Percent contents, %
MnO_2	10,72	10,72
Mn_2O_3	0,42	0,42
$CaCO_3$	77,05	77,05
Fe_2O_3	3,73	3,73
Al_2O_3	1,19	1,19
SiO_2	4,75	4,75
$MgSiO_3$	2,14	2,14
Total:	100	100

Composition of carbonate ore during introduction of chlorine is presented in Table 1.

During introduction of a certain amount of chlorine into water suspension of carbon- ate manganese ore in order to receive HCl, mass of which equals 100 g, destruction of ore with receipt of the corresponding products takes place.
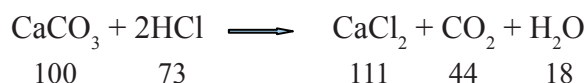
Table 2

The amount of product destruction in ore after introducing chlorine into suspension of carbonate manganese ore and formation of reaction products

Mass, g (MnO_2)	Mass, g(Cl_2)	Mass, g (H_2O)	Mass, g $(CaCO_3)$	Mass, g $(CaMnO_4)$	Mass, g $(CaCl_2)$	Mass, g (CO_2)
0,06	0,1	0,03	0,21	0,11	0,16	0,09
0,09	0,15	0,04	0,32	0,17	0,23	0,14
0,19	0,3	0,08	0,63	0,33	0,47	0,28
0,37	0,6	0,15	1,27	0,66	0,94	0,56
0,77	1,25	0,32	2,64	1,87	1,95	1,16
1,53	2,5	0,63	5,28	2,75	3,91	2,32
3,06	5	1,27	10,56	5,49	7,82	4,65
6,12	10	2,54	21,13	10,99	15,63	9,3
9,18	15	3,8	31,69	16,48	23,45	13,94
10,71	17,5	4,44	36,97	19,23	27,36	16,27
12,24	20	5,07	42,25	21,97	31,27	18,59

Chemism of calcium carbonate destruction process during introduction of chlorine into sus- pension of carbonate ore for stabilization of pH solution is presented as the following reacion:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$
$$100 \qquad 73 \qquad\qquad 111 \quad 44 \quad 18$$

During introduction of a certain amount of chlorine, a certain amount of chlorous cal- cium $(CaCl_2)$ forms. The results are provided in Table 3.

Table 3

Dependence of chlorous calcium formation (grams) on the introduced chlorine into the system for destruction of calcium carbonate

Mass, g $(CaCO_3)$	Mass, g (Cl_2)	Mass, g $(CaCl_2)$
24,65	17,5	27,36
21,13	15	23,45
14,12	10	15,67
7,05	5	7,82
3,52	2,5	3,91
1,76	1,25	1,95

Thus, solution of manganese oxide salt and chlorous calcium is retrieved from carbonate ore. This is how retrieving of manganese ox- ides are retrieved from ore. Disproportion of salt with receipt of $Ca(MnO_4)_2$ and MnO_2 takes place in the solution. Oxidation of one mole- cule due to another molecule of the same sub- stance is a common phenomenon in chemistry. It always goes on along with losses of free en- ergy that is possessed by the system initially. Independent reaction is defined by the fact that free energy of the system in the end of reac- tion is lower than it was in the beginning of it. Condition, described by the lowest amount of energy is the most stable.

Under a careful examination one can see that flow of a chemical reaction is not defined by general amount of energy, but free energy.

Table 4

Dependence of manganese compounds lixiviation on addition of chlorine into reaction area

Composition of manganese ore	Initial composition of manganese ore		Composition of manganese ore after its lixiviation with chlorine		Dependence of manganese ore composition on amount of the introduced chlorine		Dependence of manganese ore composition on amount of the introduced chlorine		Dependence of manganese ore composition on amount of the introduced chlorine		Dependence of manganese ore composition on amount of the introduced chlorine	
	Mass, g	Percent contents, %	Mass, g	Percent contents, %	Mass, g	Percent contents, %	Mass, g	Percent contents, %	Mass, g	Percent contents, %	Mass, g	Percent contents, %
MnO_2	10,72	10,72	0,02	Remains	1,55	2,64	4,61	6,37	7,67	8,92	9,2	9,9
Mn_2O_3	0,42	0,42	Remains	Remains	Remains	0	Remains	0	Remains	0	Remains	0
$CaCO_3$	77,05	77,05	40,08	77,26	45,35	77,26	55,92	77,31	66,48	77,35	71,76	77,39
Fe_2O_3	3,73	3,73	3,73	7,19	3,73	6,35	3,73	5,16	3,73	4,34	3,73	4,02
Al_2O_3	1,19	1,19	1,19	2,29	1,19	2,03	1,19	1,65	1,19	1,38	1,19	1,28
SiO_2	4,75	4,75	4,75	9,15	4,75	8,08	4,75	6,56	4,75	5,52	4,75	5,11
$MgSiO_3$	2,14	2,14	2,14	4,11	2,14	3,64	2,13	2,95	2,13	2,49	2,14	2,3
Total:	100	100	51,9	100	58,71	100	72,33	100	85,95	100	92,77	100

The fact that calcium manganite solution of manganese acid, in which manganese valency equals six, decomposes easily, point us to the conclusion that free energy in a system that consists of four- and seven-valent manganese, is lower than free energy that is contained in a system that keeps all manganese in six-valent form. However, conditions are usually opposite, and the state of intermediate valency proves to be the most stable condition. Thus, permanganate and salt of bivalent manganese react and form four-valent manganese.

Conclusion

While analyzing the research results, we can establish a possibility of simultaneous receipt of permanganates with the following obtaining of highly-concentrated manganese dioxide of no less than 85 %, as well as possibility of retrieving only manganese oxides from impoverished carbonate ore.

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