Tsvetnye Metally
2012, No. 9, pp. 52–55

Efficiency of oxide compounds of magnesium in purification of alumina industry solutions from organic impurities

UDC 669.712.15

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The Bayer process aluminate solutions are characterized by accumulation of organic compounds, which worsen the manufacturing parameters and quality of produced alumina. Sorption methods of purification are the easiest and the most efficient. Sorption characteristics of activated carbon, magnesium oxide, hydrated carboaluminates and sulfoaluminates of magnesium are considered, concerning organic chemistry of aluminate solutions. Extra-sorbtion mechanism was defined during the processing of aluminate solutions by activated magnesia. There was also defined the high sorption potential of magnesium hydroaluminate phases. Advantages of such compounds consist in the following factors:
– likeness of sorbent composition to the system;
– absence of influence on solution's technological structure;
– low power expenses for reagent regeneration (at the temperatures of 250–400 °C).
The foregoing characteristics of synthesized sorbents can be the basis for development of technology of aluminate solutions purification from organic compounds by active sorbents (hydrated carboaluminates and sulfoaluminates of magnesium).

Key words: aluminate solutions, hydrated carboaluminate of magnesium, sorption, purification of solutions, organic impurities, the Bayer process.

One of the problems of alumina industry is a presence of organic compounds in aluminate solutions during the obtaining of aluminium hydroxide from bauxites, according to the Bayer process.

Presence of these substances is connected with the following phenomena and technological problems:

– decreasing of precipitation degree of aluminate solution;

– lower alumina quality;

– decreasing of ratio of hydrometallurgical equipment utilization;

– intensive foaming;

– worsening of physical properties of solutions (increasing of density and viscosity; solutions get the indicative red-brown color).

The quality of processed alumina is of the highest priority in modern market conditions, when every tenth of percent of produced aluminum is got with struggling. At the same time, the task of organic compounds control in aluminate solutions of alumina industry comes to the fore and attracts more researchers to its solution.

It is well-known that contact of aluminate solution with various magnesium compounds (MgO, $Mg(OH)_2$, $MgSO_4$ etc) favorably affects the quality of produced alumina and technological parameters in whole, which is explained by high sorption activity of added and new-formed substances, according to the dissolved impurities [1–5].

In connection with this fact, it is interesting to investigate the behavior of hydrated carboaluminate of magnesium as an individual sorbent in relation to organics of aluminate solutions. Such type of compounds has the following advantages:

– elimination of joining of Al_2O_3 in insoluble compounds leads to absence of changes in composition of technological solution;

– energy-saving technology of sorbent's regeneration.

According to organics of aluminate solutions, obtained from the processing of torrid zone bauxites by Bayer process, there was carried out the set of experiments for determination of sorption activity of calcined magnesia, hydrated carboaluminates of magnesium (HCAM), hydrated sulfoaluminates of magnesium (HSAM) and activated carbon (C_{act}) (as the most popular sorbent).

Aluminate solution of Nikolaev Alumina Refinery was chosen for investigation (Nikolaev Alumina Refinery processes Guinea and Australia bauxites).

Magnesium oxide was manufactured by hydroxide calcination at the temperature of 600 °C during 2 hours.

Synthesis of a sample of hydrated aluminate of magnesium was carried out, using the magnesium oxide ("ch" ("ч") grade). Aluminate-alkaline solution was manufactured by dissolution of Al powder in alkali (250–260 g/l). Na_2CO_3 and Na_2SO_4 were the source of carbonate-ions and sulfate-ions, respectively. The synthesis was carried out in thermal-resistance crucible by intensive mixing (n = 1,400 min^{-1}), during 6 hours, at the temperature of 80 °C. The composition of sorption pulp is given in the Table 1.

75 cm^3 of aluminate solution, produced by Nikolaev Alumina Refinery, was poured into the porcelain crucible. At the same time, sorbent was added under intensive mixing condition. After the required thermostating period, residue was filtered and cake was dried at the temperature of 100 °C. Filtrate was analyzed for determination of organic and Al_2O_3 quantity.

The content of colored organic compounds was determined by photometry, based on measurement of optic den-

Table 1
Composition of pulp of synthesized HCAM and HSAM

Compound	Concentration, g/l	
	HCAM	HSAM
Al_2O_3	85	85
MgO	200	200
Na_2O_k	258	250
CO_3^{2-}	30	–
SO_4^{2-}	–	60
Total in a solid phase	315	345

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sity of investigated solution. Measurements were carried out on the Leki SS 1207 UV spectrophotometer with the wavelength (l) of 440 nm. Previously, the solution was diluted by 10 times. Direct connection between optical density of solution and content of colored organic compounds was estimated. Photometry was chosen as a basis for investigation of purification efficiency, because it differs from other methods by its quickness, accuracy and reproducibility of adequate results.

Experimental conditions and data about sorption of organic compounds and Al_2O_3 from solutions are given in the Table 2.

The main criteria during the choice of one or another sorbent type is its sorption activity, which depends on its nature and selectivity. Sorption activity complies with well-known physical and chemical laws (in this investigation it will be expressed by weight of sorbed material per one gram of sorbent, mg/g). This characteristic is qualitatively fitted to adsorption isotherm and is mathematically stated by Langmuir equation:

$$a = a_\infty KC/(1 + KC),\ \text{g/g}, \qquad (1)$$

where: a_∞ – a maximum of sorption activity for this type of sorbent, g/g; K – a sorption constant; C – an adsorptive concentration, g/l.

For the purpose of experimental determination of characteristics of a_∞ and K, it is necessary to convert the Langmuir equation into linear form:

$$C/a = 1/(K{\cdot}a_\infty) + C/a_\infty. \qquad (2)$$

Maximum sorption activity and its constant were determined for each sorbent (Fig. 1). Linear connection makes it possible to determine the equation coefficients $1/(K{\cdot}a_\infty)$ and $1/a_\infty$ (2). Theoretical maximum sorption and constants are given in the Table 3.

According to obtained data of K and a_∞, adsorption isotherms were created for each of the foregoing sorbents (Fig. 2).

On the basis of analysis of maximum sorption's coefficient and characteristic isotherm lines, it can be surely stated that in comparison with such sorbents like universal activated carbon or MgO (well-known sorbent in alumina chemistry), the synthesized hydrated carboaluminates and sulfoaluminates of magnesium have substantial sorption activity. However, it should be noted that, according to contaminants, such activity is necessary but insufficient criterion for development of efficient method of aluminate solutions purification.

Reagent should be chosen from a point of the lowest economic costs for its purchase or recovery; possibility of its secondary using; similarity to the system and the lowest effect on qualitative and quantitative composition of aluminate solution.

Application of activated carbon in real production processes is impossible because of a hard

Table 2
Parameters of sorption purification of aluminate solutions

Experiment	Sorbent	m_s, g	t, °C	τ, min	m_s of COC, mg	$DmAl_2O_3$, g	m_c, g
1	MgO	10	20	10	684	0.10	11.20
2		10	40	10	702	0.05	10.90
3		10	60	10	839	0.40	12.20
4		10	80	10	918	1.63	20.20
5		10	80	5	522	0.60	12.30
6		10	80	20	774	1.19	17.60
7		10	80	30	972	2.45	21.70
8		10	80	60	1107	3.85	24.40
9		10	80	180	1224	4.20	26.07
10	HCAM	9	20	10	756	0.01	9.90
11		9	40	10	693	–	8.50
12		9	60	10	630	–	9.40
13		9	80	10	432	0.15	6.90
14		6	20	10	810	–	7.10
15		4	60	30	468	–	4.30
16		3	30	20	450	–	3.60
17		9	20	30	756	0.30	9.45
18		9	20	5	711	–	9.70
19	HSAM	9	20	10	832	–	9.90
20		9	40	10	738	–	9.50
21		9	60	10	666	–	10.10
22		9	80	10	396	–	9.46
23	C_{act}	8	20	10	1199	–	–
24		8	40	10	882	–	–
25		8	60	10	45	–	–
26		8	80	10	324	–	–

m_s – sorbent mass; m_s of COC – sorbent mass of colored organic compounds; m_c – cake mass.

Table 3
Results of determination of sorption coefficients

Type of sorbent	Graphic characteristics		Calculated data	
	$1/a_\infty(x/y)$	$1/(a_\infty{\cdot}K)$	a_∞, mg/g	K
MgO_{act}	0.0078	0.107	128.6	0.0727
HSAM	0.0069	0.100	145.2	0.0688
HCAM	0.0061	0.168	163.9	0.0363
C_{act}	0.0054	0.031	184.2	0.1750

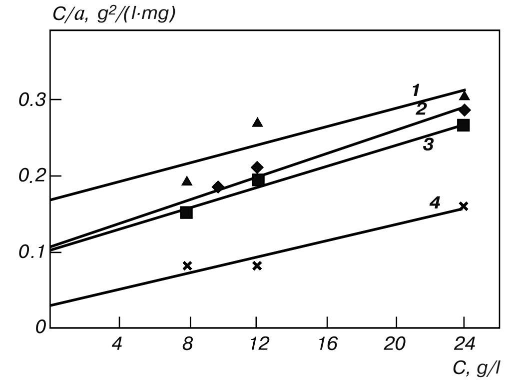

Fig. 1. Diagram of experimental determination of constants in Langmuir equation (room temperature, t = 10 min, mixing at n = 120 min^{-1}):
1 – HCAM; *2* – MgO; *3* – HSAM; *4* – C_{act}

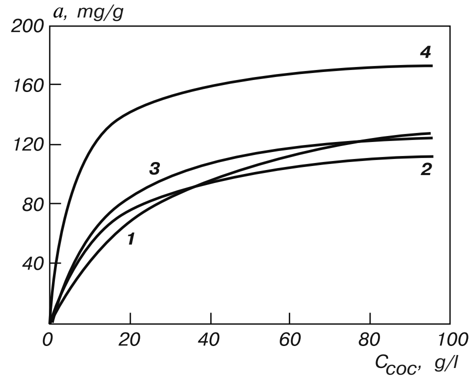

Fig. 2. Adsorption isotherms of colored organic compounds for different sorbents:
1 – HCAM; *2* – MgO; *3* – HSAM; *4* – C_{act}

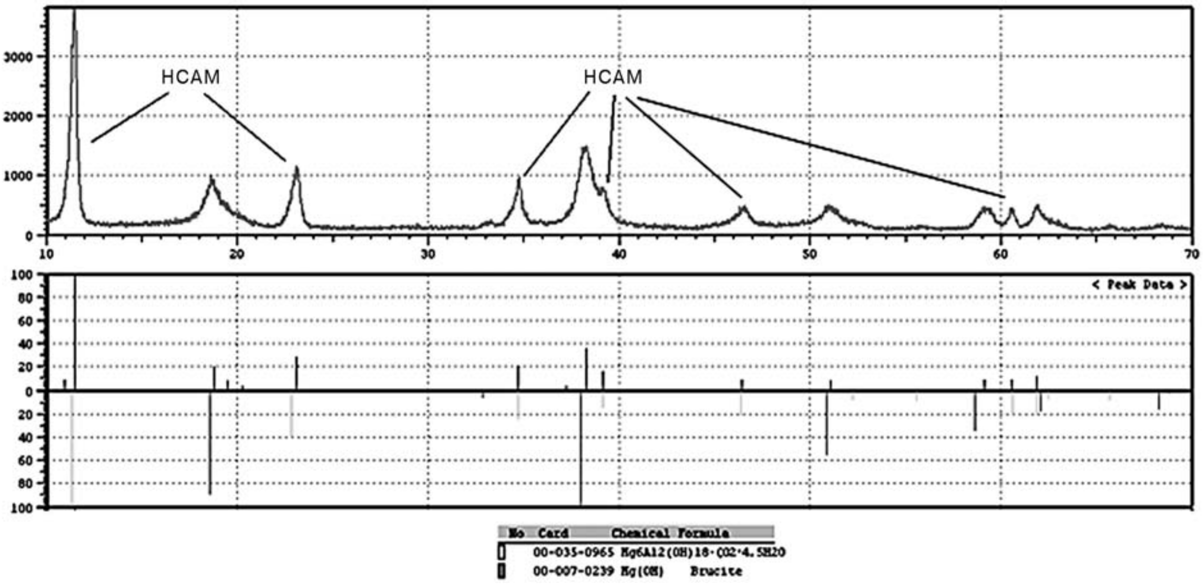

Fig. 3. X-ray diffraction pattern of a solid phase received after treatment of aluminate solutions by magnesium oxide (experiment No. 9)

constraint for impurities and absence of natural sorbent's regeneration possibility.

According to received data, magnesium oxide is also efficient for purification of aluminate solutions from colored organic compounds at room temperature. However, most authors note [1, 4–8] that sorption activity clearly appears when temperature is higher. It can be explained by activation of ion-exchange processes and formation of new structures. The highest indices were obtained at the temperature of 80 °C, which substantially is optimal for synthesis of hydrated aluminates of magnesium. According to X-ray phase analysis of dried cake, after sorption of aluminate solution organics (Nikolaev Alumina Refinery) at the temperature of 80 °C (Fig. 3), it is confirmed that the process is carried out with formation of essential quantities of hydrated carboaluminates phase (sharp peak: $2\theta = 11.8°$).

In the context of adsorption theory, the temperature increase makes a direct influence on the process by increasing of desorption rate (decreasing of adsorption) in consequence of rising of thermal Brownian motion of particles, which tends to uniform distribution of the material in the whole volume. This behavior was detected for all types of sorbents, except activated magnesia (Fig. 4). Uncharacteristic response of MgO sorbent on temperature increase is a result of

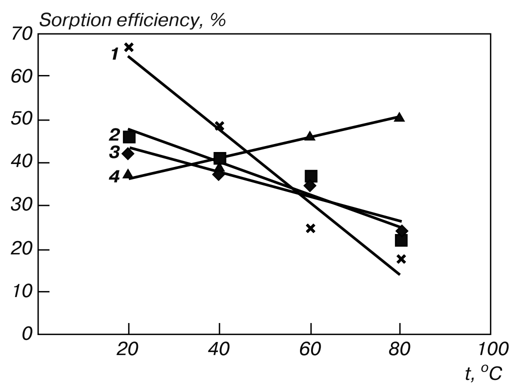

Fig. 4. Temperature effect on sorption efficiency:
1 – C_{act}; *2* – HSAM; *3* – HCAM; *4* – MgO

new-formed structures (HCAM) action. However, the stage of involvement of these structures cannot be felt in production conditions.

Consequently, the considered high sorption activity of MgO at the temperatures of 60–90 °C is not objective because in this case, additional sorption potential (extra-sorption) is provided by formed hydrated aluminate phases. Moreover, it should be taken into account that this process is accompanied with the change in solution's composition – weight of fixed and excluded Al_2O_3 into residue is about 0.3–0.5 gram per each additional gram of MgO (Table 2).

For this reason, received high sorption characteristics of hydrated carboaluminates and sulfoaluminates of magnesium (results of reaction between MgO and alkali aluminate solutions) deserve a special attention. Communication of these characteristics with solutions is not connected with alumina losses and change in structure.

Moreover, the regeneration stage of such sorbents does not require high energy consumptions (250–400 °C instead of 600–900 °C for magnesia activation), which is a good prospect for the development of efficient scheme and makes it possible to close a purifying branch of technological cycle, during the development of technology of organic compound's excretion.

Conclusions

High sorption activity of magnesium-containing compounds (calcined magnesia, hydrated carboaluminates and sulfoaluminates of magnesium) is identified for organic compounds in aluminate solutions.

In the conditions of alumina production, it is important that hydrated carboaluminates and sulfoaluminates of magnesium are also active sorbents for colored organic compounds. In addition, realization of this production becomes easier due to absence of necessity for special conditions (sorbent is active both at the temperature of 60 °C and at the room temperature, and the process is finished in approximately 5 minutes). Regeneration of sorption activity of HCAM and HSAM can be carried out without high energy consumption at the temperature range of 250–400 °C, which deserve special attention.

All the foregoing is a good precondition for development of technology of purification of aluminate solutions from organic compounds by active sorbents – hydrated carboaluminates and sulfoaluminates of magnesium.

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