Intensification carboaluminate technology of ultradeep desiliconization

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Abstract. The article presents the results of the study of the effect of additive hydrogarnet sludge on the process of carboalumination desiliconization of aluminate solution. It is proved that type-ahead hydrogarnet sludge significantly intensifies the process of ultra-deep desiliconization due to the catalytic effect of the surface of the slurry in accordance with the theory of heterogeneous catalysis. A mathematical process model for the process of superdeep desiliconization in increased turnover hydrogarnet sludge is presented.

1. Introduction

As a result of numerous experimental works [1-4], universal principle of activating effect on the deep desiliconization of hydrogarnet sludge introduced into the aluminate solution with some advance before direct interaction response of the gysraulic carbo-aluminate calcium with silicas [5-7]. This principle has been verified on various aluminate solutions and carbo-aluminates synthesized on the basis of carbonate raw material of the automated hydrological complex (Mazulskoye, Kiya-Shaltyrskoye limestone fields), under-gas-cap zone (Pikalevskoye field), a number of foreign fields.

The analysis of the above mentioned works suggests that new processing ways of by-products in a complex processing of nepheline raw material are:

The simplified version of this principle was tested in laboratory and in field simultaneously and for multiple times, with simultaneous introduction of the hydrogarnet sludge and calcium carbo-aluminate, and as a result it was proven demonstratively that there is no activation effect of the deep desiliconization response [8].

The advance introduction of the hydrogarnet sludge significantly intensifies the ultradeep desiliconization process. With the HCAC flow rate of 7 g/l by CaO\textsubscript{act.} and 100% turnover of the hydrogarnet sludge, ~ 30 g/l on hard, for real time of commercial desiliconization (2 hours) at "PGZ-SUAL" branch reaches the value of silicon module at the level of 4,000-5,000 units, and the alumina release, grade G-000 (SiO\textsubscript{2} – 0.02%; Fe\textsubscript{2}O\textsubscript{3} – 0.01% reaches 100%.

Our studies show that due to the increased turnover of the hydrogarnet sludge yo 50 g/l on hard the silicon module can be brought to 10,000 units and more (i.e. to the traces) without increasing the HCAC flow rate.
Figure 1 shows the dependence of the depth of desiliconization at the existing commercial flow rate of carbo-aluminate of 7 g/l by CaO\textsubscript{act}. From the amount of the white sludge seed.

**Figure 1.** Catalytic properties of hydrogarnet sludge during carboalumination desiliconization

1 – joint input of non-ignition HCAC and circulating hydrogarnet sludge;
2 – advanced circulating hydrogarnet sludge input.

HCAC dosage ~ 7 g/l by CaO\textsubscript{act}.

It should be noted that bringing the SiO\textsubscript{2} additive in the alumina solution to the traces significantly simplifies the task of producing active sandy alumina (hydroclassification of aluminum hydroxide, efficient use of large and small seeds, respectively, in the soda branch and at the stage of agglomeration in the alkali branch, reduction of α-Al\textsubscript{2}O\textsubscript{3} to 6-8%, etc.) The reduction of the SiO\textsubscript{2} addition to the traces increases specific surface of Al\textsubscript{2}O\textsubscript{3} from 60 to 80 g/m\textsuperscript{2}, and the flow ability by 1.5 times (the natural angle of slope reduces from 36 – 37 degree to 33 degree). This is due to the Al (III) hydroxocomplex structure and sharp decrease in the intensity of proton exchange between the Al (III) and Si (IV) ions that facilitates the Al(OH)\textsubscript{3} agglomerate growth due to intensified agglomeration of gibbsite radicals by "long" polymerization (Si (IV) hydroxocomplexes break the polymer chains Al(OH)\textsubscript{6}\textsuperscript{3-}, focusing them in inter-cluster space by dissolving on the alumina solution cluster surface) that corresponds to literature data on structural peculiarities of concentrated alumina solutions.

The intensification of the aluminate solution deep desiliconization by preliminary introduction of return hydrogarnet sludge with further alumina and carboalumina calcium interaction is related, on our opinion, to catalytic interaction of the solid body surface (catalyst), i.e. return sludge. This hypothesis has several features characteristic for a number of elements of the theory of heterogeneous catalysis [9-12]:

1. The apparent activation energy of the deep desiliconization response with the introduction of return hydrogarnet sludge decreases almost twice from 96 kJ/mole to 50 kJ/mole [1].

2. Gibbs energy change for the hydrogarnet formation response [2-3] calculated by structured analogy method [4] is less than 0 (complex heterogeneous catalysis processes can flow in several directions through the interim processes but in any case the condition ΔG < 0 should be observed for the whole process).

3. The main role in accelerating the desiliconization response play active centers of the hydrogarnet sludge; the sludge specific surface is small, ~3.5 m\textsuperscript{2}/g, it is rather less the specific surface of carbo-alumina phase; even the hydrolysis traces in particular areas of hydrogarnet sludge, when the whole sludge surface is free from passivating aluminum hydroxide films, lead to deactivation of desiliconization response.
4. From the point of view of the theory of heterogeneous catalysis, not only active centers but also their arrangement are important, the so-called principle of geometric conformity requiring the similarity both of distances, and main elements of the symmetry of the formed molecule and catalysts. If there is no such similarity, the process will not accelerate [9].

Actually, during the hydrogarnet sludge change, for example, for active aluminum hydroxide with the high-developed surface or for any other active seed, the intensification effect of the deep desiliconization response disappears.

The role of the geometry principle, entropic factor in heterogeneous catalysis regarding the considered desiliconization process is also confirmed by the accelerating effect of the preliminary electric treatment of aluminate solutions on this process resulting in changing configuration of aluminum (III) and silicon (IV) hydroxocomplexes, thus bringing the system to formation of the relevant quasi-seed domain groups which are similar to hydrogarnet.

When describing the macroprocess of the carboaluminate interaction with alumina in the aluminate solution with the advance introduction of return sludge, it should be clearly represented that the sludge effect on this process does not change its main essence: SiO$_2$ reaction with hydrated calcium carboaluminate occurs when the rate of isomorphic exchange $4$(OH)$^-$→[SiO4]$^4$ is comparable with the rate of rearrangement of hexagonal metastable carboaluminate lattice in the cubic hydrogarnet lattice.

The return sludge active centres only create the best conditions by forming the interim complex to reduce steric hindrances in the isomorphic exchange mentioned.

2. Mathematical modelling of the aluminate solution of deep desiliconization process with preliminary introduction of hydrogarnet sludge

To prepare the automatic process control system [14-19] of the deep desiliconization process in increased return of hydrogarnet sludge, the corresponding mathematical model was developed [20-23]. In the frameworks of the general desiliconization model, in the presence of HCCA, the desiliconization with preliminary addition of the white sludge can be considered as the interaction of the silicon ion and HCCA occurred in the kinetic area. The hydrogarnet formation kinetics equation corresponds to such process:

$$\frac{dM}{dt} = K \cdot A^m \cdot C_{\text{Si}}^{n}$$

(1)

where $M$ - the amount of precipitated hydrogarnet, (g/l),

$K$ – chemical reaction rate constant,

$A$, $C_{\text{Si}}$ – concentrations of calcium carboaluminate (for CaO) and silicon (for SiO$_2$), respectively (g/l),

$m$, $n$ – reaction orders for CaO and SiO$_2$.

For the offered mathematical model identification (determination of the reaction rate constant $K$ and reaction orders $m$, $n$), the laboratory experimental data were used. The experiments were conducted with aluminate solutions of the chemical composition that correspond to the conditions of stage II desiliconization of "PGZ-SUAL" branch, with the added 30 g/dm$^3$ of white sludge and 30-60 min. exposed suspension. The HCCA sample weight was varied within the range of 2.5 g/l CaO and the temperature within 70-98°C. Equation integration (1) considering the balance formula:

$$M = C_{\text{Si}}^0 - C_{\text{Si}}$$

(2)

where $C_{\text{Si}}^0$ is initial concentration SiO$_2$,

$$\frac{1}{(n - 1) \cdot A^m} \cdot \left( \frac{1}{(C_{\text{Si}}^0)^{n-1}} - \frac{1}{C_{\text{Si}}^{n-1}} \right) = Kt \quad \text{for } n \neq 1$$

(3)

$$\frac{1}{A^m} \cdot \ln \frac{C_{\text{Si}}^0}{C_{\text{Si}}} = Kt \quad \text{for } n = 1$$

(4)

These expressions were balanced with substitution of variables $C_{\text{Si}}^0 \rightarrow y$ of the type
\[ y = \frac{1}{(n-1) \cdot A^m} \cdot \left( \frac{1}{C_{Si}^0} \cdot n^{-1} - \frac{1}{C_{Si}^{-1}} \right) \quad \text{for } n \neq 1 \] (5)

\[ y = \frac{1}{A^m \cdot \ln C_{Si}^0} \quad \text{for } n = 1 \] (6)

It appeared that with \( n = 1 \) in the most experiments, the dependence curves \( y(t) \) differ from the straight line and have the distinct up convexity, and with \( n = 2 \) – down convexity. That is why we took the reaction order for \( \text{SiO}_2 \) as \( n = 3/2 \). Then, to determine the reaction order for \( \text{CaO} \), the nature of families of curves \( y(t) \) for various HCCA sample weights at the unchanged temperature of the desiliconization process. \( m = 3/2 \) was taken, when the minimum divergence of slope ratios of curves \( y(t) \) was observed. Thus, the kinetic equation becomes (see(3))

\[ \frac{2}{A^{3/2}} \cdot \left( \frac{1}{C_{Si}^{0(1/2)}} - \frac{1}{C_{Si}^{-1/2}} \right) = Kt \] (7)

Or explicit

\[ C_{Si}(t) = \frac{C_{Si}^0}{((1 + 1/2K \cdot A^{3/2}(C_{Si}^0)^{1/2} \cdot t)^2} \] (8)

Dependence of the reaction rate constant \( K \) and temperature \( T \) in the form of the Arrhenius equation.

**Figure 2.** Kinetic regularities of interaction \( \text{SiO}_2 \) with HCAC, \( \text{CaO} \) и \( \text{C}_3\text{AH}_6 \) in aluminate solution

\[ \text{Al}_2\text{O}_3 - 90 \text{ g/l}, \alpha_c = 1.5; \text{Dosage} \frac{\text{CaO}_{\text{act}}}{\text{SiO}_2} = 6 \]

1 – \( \text{C}_3\text{AH}_6 \) (75 °C); 2 – \( \text{CaO} \) (75 °C); 3 – HCAC (75 °C); 4 – HCAC (90 °C);

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Experimental data

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Theoretical data

Processing of the measured values (slope ratios of curves \( y(t) \)) for this equation has provided:
activation energy $\Delta E = 50.16 \text{ kJ/mole}$

ratio $K_0 = (1.32 \pm 0.2) \cdot 10^7$

To compare, it should be noted that the activation energy determined under the same conditions for the hydrogarnet formation response is equal to 55.88 kJ/mol that is rather close to the measured value.

Figure 2 shows the experimental and calculated by equations (8) and (9) kinetic dependences $C_{Si}(t)$ for $T = 353K$.

The model verification according to the experimental data [16] showed that it is adequate to the describe process according to the Fischer test.

3. Conclusions

As a result of preliminary input additive circulating hydrogarnet sludge may significantly increase the depth and speed of desiliconization of aluminate solutions. The reason for the intensification of the process of ultra-deep desiliconization is a catalytic effect of the surface of the sludge, the active centers which create the best conditions for interaction via formation of an intermediate complex to reduce problems with isomorphic $4(\text{OH}) \leftrightarrow [\text{SiO}_4]^{4-}$.

Mathematical model of the process of desiliconization involving hydrogarnet sludge were identified according to laboratory experiments, when it was created was determined magnitude of the rate constant and reaction order.

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