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TECHNOLOGY OF ORGANIC AND INORGANIC CHEMISTRY

Studying an Effect of Reaction Furnace Operation Regime on a Fluoroanhydrite (Anhydrite Gypsum) after the Furnace

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Abstract—Results of the study under plant conditions of the operation regime effect of the reaction furnace on composition and cementing properties of the fluoroanhydrite are presented in this paper. On the basis of data obtained on the first stage of the study of the reaction furnace operation regime a comparative analysis of second stage data was carried out, and also recommendation for an improvement of a main equipment was set out.

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Storing a solid waste of hydrofluoric manufacture OAO "Polevskii Kriolitovyi Zavod" on a sludge tanks is one of the way of an environmental disturbance in the Sverdlovsk region. Manufacturing hydrogen fluorine is based on an interaction between a natural mineral, fluor spar, enriched by calcium fluoride, and concentrated sulphuric acid at high temperature (~900 °C).

This technology proceeds with formation of calcium sulfate waste or the fluoroanhydrite (FA) according to reaction:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Nowadays $CaSO_2$ mainly as low-activity modification: insoluble fluoroanhydrite containing in addition to non-decomposed CaF_2, SiO_2, and sesquioxides also free H_2SO_4, adsorbed HF is neutralized by a limestone pulp and then is dumped in the slime fields. According to [1–7] an experience of an application of the fluoroanhydrite as a cementing addition (agent of mineralization, regulator of the cementation time), as a pigment etc occurs both in our country and abroad. Use of FA is complicated by an instability of composition caused evidently by a decomposition regime of the fluor spar, therefore we set a problem of studying dependencies showing the effect of the fluoric concentrate decomposition regime on physicochemical and cementing properties of the fluoroanhydrite, and also on the neutralization, grind, and aquation at solidification.

The first stage of the study on revealing the dependencies that show the effect of the fluoric concentrate composition, and sulphuric acid, and also the decomposition regime of the fluor spar on the fluroranhydrite quality is performed both by OAO "PKZ" and by Ural Polytechnic Institute in 1994 on the area of a furnace room. In the course of the study hourly sampling of the furnace outlet fluoro-anhydrite occurred, also such parameters as an output of the fluoroanhydrite concentrate, and sulphuric acid, CaF_2 amount in the concentrate, and its size composition, temperature of the furnace output fluroanhydrite, an amount of CaF_2 and H_2SO_4 in the fluoroanhydrite, and also the fluoroanhydrite cementing properties were analysed. Characteristics of a reaction furnace feed, and also physicochemical properties of a raw and the fluoroanhydrite are presented in Table 1. The hot acid fluoroanhydrite was ground by a pilot crusher of the furnace room simultaneously feeding preliminary ground quicklime of an amount required for sulphuric acid neutralization with 5 wt % excess with respect to stoichiometric computed value. A grind time was permanent. The ground fluroanhydrite was stood 2 and 7 days for an efficient neutralization with sulphuric acid.

The amounts of free CaO and H_2SO_4, also H_2O_{cryst} in 2 and in 7 days of the standing, the cementation time, a breakup by checking an amount of a residue on a sieve (a sieve type no. 008) were measured for the neutralized product. The ground and neutralized fluoroanhydrite of the various standing time was mixed with water to

Table 1. Physicochemical properties of the raw and the fluoroanhydrite, the furnace feed

Raw			Furnace feed		Fluoroanhydrite after the furnace		
fluorite		sulphuric acid	fluorite	sulphuric acid	temperature, °C	chemical composition, wt %	
Residue on the sieve no. 14	CaF_2	H_2SO_4, wt %	t/h	t/h		CaF_2	H_2SO_4
Reaction furnace no. 1							
1.00–8.40	91.7–96.0	91.71–92.85	9.50	13.13–14.59	225–310	0.81–5.84	1.46–12.00
Reaction furnace no. 2							
1.36–6.92	91.6–96.8	91.64–92.49	9.00	13.86–14.59	210–275	1.26–5.89	2.81–12.49

a normal water consumption and then bar-samples of size 4 × 4 × 16 cm were formed and stood under room conditions. The bar-samples were tested for strength in 7 and 28 days of solidification.

A mathematical treatment of the data showed:

(1) The amount of CaF_2 in the fluorite concentrate varies in the wide range as the manufacture applies simultaneously mixtures of concentrates from Yaroslavl, Chine, and Mongolia. Dispersion in a dosage of H_2SO_4 up to 5.0 and 10.0% is noted in the first and second reaction furnaces, respectively;

(2) A decomposition rate of the fluorite concentrate significantly depends on a ratio between H_2SO_4 and CaF_2 in the fluorite, a fluorite dispersity, and a temperature of reaction environment. It was established that the decomposition rate of the fluorite decreased and more amount of H_2SO_4 and CaF_2 transferred in FA at increase of the large size fraction in the fluorite (>0.1 mm).

(3) The neutralization rate of H_2SO_4 at the constant excess of CaO depends on the H_2SO_4 concentration in the initial fluoroanhydrite. The neutralization efficiency is 99.0% achieved for lesser neutralization time in the case of high amount of H_2SO_4 (>10 wt %). In the case of H_2SO_4 concentration lesser than 3.0 wt % the neutralization efficiency is not higher than 94 and 97% at 2 and 7 days of the standing, respectively.

(4) An amount of the unreacted H_2SO_4 is proportionate to the fluoroanhydrite dispersity. Thus the grind when the amount of the fraction of +01 mm is not more 5.0 wt % is required for obtaining the fluoroanhydrite with H_2SO_4 amount <0.05 wt %.

(5) Water/hardness ratio of the neutralized fluoro-anhydryte increases at the free H_2SO_4 growth as H_2SO_4 is an effective accelerator of the cementation besides this ratio increases at the smaller grain-size of FA.

(6) The cementation time of the neutralized FA reduces at a growth of secondary $CaSO_4$ amount, and respectively, H_2SO_4 amount in the initial FA, and also at the process temperature decrease. The average value of the cementation time: start of cementation time is 5–7 h, and finish of the cementation is 8–12 h (however in the some cases the cementation time achieves 17–19 h).

(7) Pressure strength reduces at CaF_2 amount increase in the FA. The growth of H_2SO_4 amount in the initial FA (>7.0–9.0%) and, respectively, of secondary $CaSO_4$ amount significantly reduces a break point. Increase in the water/hardness ratio also reduces the break point. The average value of the break point of samples regardless of the standing time in 28 days of the cementation is 9.0–11.0 MPa, however a part of these values ranges in 15.0–16.0 MPa.

(8) The H_2SO_4 amount in the initial fluoroanhydrite effects on the aquation of the neutralized FA. It was found that in the range of the H_2SO_4 concentration of 3.0–6.0 wt % the sufficiently large aquation efficiency of FA reached: H_2O_{2cryst} amount was 15.0–17.0 wt %.

Measuring the cementing property of FA formed from the fluorite concentrate at the study including the mixing, cementation, solidification and aquation we found that the decomposition regime of the fluorite concentrate should supported at the following characteristics at the furnace outlet: the FA temperature is not more than 260–270°C, the H_2SO_4 amount is 3.0–7.0 wt %, the amount of CaF_2 is not more than 3.0 wt %.

For enhancement process we suggested some recommendations. According to these recommendations since 1995 the manufacture heated the sulphuric acid to 60°C that enhanced reaction of the sulphuric acid

with fluoric concentrate in an agitator-screw and thus most complete interaction of the reagents in the reaction furnace was provided. Besides a gas-jet GVP-3 in the second reaction furnace was substituted by more effective gas-jet GRDP-8-2 that enables governing a torch flame length providing more qualitative agitation of air and natural gas and as a result more complete proceeding the reaction of the main components and reducing their output in the fluoroanhydrite. Last 7 years OAO "PKZ" uses the raw of either or other deposit e.g. Mongolian raw or Yaroslavl raw, of an approximately permanent dispersion composition.

We performed the second stage of the study of the hot FA samples for estimation of an influence of introduced changes in the technological regime of the fluor spar decomposition on the studied characteristics of the FA after the reaction furnace. The sample was carried out for one shift. In this period the manufacture used the fluoric concentrate of the Yaroslavl deposit. The parameters of the reaction furnace operation, and the physicochemical composition of the raw were presented in the Table 2.

The data of Table 2 show that the fluoric concentrate of one deposit is sufficiently stable relative to the dispersion and chemical composition that promotes reducing the dispersion of the H_2SO_4 dosage values from 10–5% to 8–1.5%, respectively for the first and second reaction furnaces in comparison with the main equipment operation using the mixture of the concentrates. The stable dispersion and chemical composition of the fluorite provided more homogeneous agitation of the fluorite and the sulphuric acid, and resulted in an increase in decomposition rate and reducing output of H_2SO_4 and CaF_2 in the FA. The preliminary heating the sulphuric acid to 60°C also decreased the amount of H_2SO_4 and CaF_2 in the FA to the recommended values of 3.0 and 7.0 wt %, respectively, due to more complete proceeding interaction between the initial components already in the agitator-screw. Replacement of the gas-jet on the second reaction furnace enabled increasing the decomposition efficiency of the fluorite concentrate to 98.0–99.0% while the decomposition efficiency of the fluorite concentrate in the first furnace was 96.0–97.0% that resulted in a decrease in the CaF_2 amount in the FA. Besides, the dispersions of the values for the amount of H_2SO_4 and CaF_2 in the FA equaled 30.0 and 20.0%, respectively. These values were practically twice less than ones in the FA after the first furnace that was evidence of sufficiently high homogeneity of the output waste from the second reaction furnace. Also with the help of the gas-jet GRDP-8-2 the decomposition temperature in the reaction furnace was correctly managed and the temperature of the fluoroanhydrite of no more than 240°C was obtained.

Cementing agent obtained by the FA according to the technique noted earlier are characterized by the physicochemical properties presented in Table 3.

The data of Table 3 shows that dependencies obtained on the first stage demonstrating an influence of the operation regime of the reaction furnaces on the physicochemical properties of the cementing agent prepared by the FA are available for the results of the second stage. However the introduced changes in the technological regime of the decomposition of the fluor spar recommended in earlier studies led to reducing the cementation time of the cementing agent prepared by the FA output from the first furnace to 10–50%, and to reducing 2–2.5 times after the second reaction furnace. The introduced changes also diminished the water/solid ratio, increased the pressure strength, increased H_2O_{cryst} amount in the cementing agent prepared by the FA output from the second reaction furnace in comparison with the

Table 2. Operation parameters of the reaction furnaces, the physicochemical composition of the raw and fluoroanhydrite

Raw			Feed of the furnace			FA after the furnace		
fluorite		H_2SO_4	fluorite	H_2SO_4	gas flow	temperature, °C	chemical composition, %	
the residue on the sieve no. 14	CaF_2, wt %	H_2SO_4, wt %	t/h	t/h	nm^3		CaF_2	H_2SO_4
>1%	93.90	94.00	The reaction furnace no. 1					
			11.5	14.54–13.80	600	226–251	1.78–2.88	3.60–5.15
			The reaction furnace no. 2					
			10.0	12.88–13.06	470	218–234	0.22–0.32	5.97–7.46

Table 3. The physicochemical properties of the cementing agent

Sample no.	Characteristics of the neutralized FA			Mixture			Cementing agent			
	H_2SO_4, wt %	CaO, wt %	residue on the sieve %	W/S ratio	cementing time, h		breakup point, MPa		$H_2O_{2\ cryst}$, wt %	
					start	finish	7 days	28 days	7 days	28 days
Reaction furnace no. 1										
1	0.10	1.71	4.20	0.41	3.50	5.90	7.00	9.50	15.45	17.00*
	0.08	1.51	4.00	0.42	4.20	5.00	7.10	9.30	15.85	16.60
2	0.09	1.50	4.40	0.41	3.90	5.65	7.00	9.35	15.40	16.90*
	0.07	1.47	4.30	0.42	4.05	5.25	7.15	9.15	15.80	16.70
3	0.06	1.45	6.68	0.44	3.10	4.85	6.40	8.90	15.50	17.10*
	0.04	1.35	6.72	0.44	3.65	4.50	6.30	8.00	15.90	16.75
4	0.11	2.15	10.50	0.42	4.10	5.85	8.20	11.30	15.37	16.80*
	0.09	2.00	10.27	0.43	4.45	5.30	7.80	9.00	15.75	16.30
5	0.13	2.40	14.10	0.42	4.50	6.50	7.80	10.50	15.40	16.50*
	0.11	2.33	13.96	0.44	4.80	6.10	8.00	10.20	15.90	15.80
6	0.20	2.75	15.47	0.44	4.50	7.10	7.00	11.00	14.56	15.84*
	0.17	2.50	15.00	0.43	5.00	7.00	8.35	11.00	14.97	15.60
Reaction furnace no. 2										
1	0.040	1.10	5.18	0.40	2.30	3.50	7.55	9.50	16.50	18.10*
	0.020	1.06	5.00	0.41	2.45	3.25	7.67	9.30	16.90	17.90
2	0.050	1.30	6.35	0.42	3.00	4.45	9.00	13.00	16.00	17.40*
	0.040	1.23	6.00	0.42	3.30	4.15	9.20	11.80	16.48	17.28
3	0.040	1.15	5.48	0.41	2.50	3.85	7.35	9.60	16.55	18.10*
	0.030	1.10	5.30	0.42	2.85	3.50	7.55	9.25	16.95	18.00
4	0.040	1.25	6.30	0.41	3.10	4.55	8.00	11.20	16.70	18.00*
	0.030	1.15	6.00	0.43	3.50	4.20	8.24	10.00	16.85	17.60
5	0.060	1.40	6.08	0.43	3.50	5.00	7.80	10.30	16.27	17.85*
	0.050	1.30	5.90	0.41	3.80	4.50	8.00	9.65	16.70	17.35
6	0.050	1.35	6.00	0.42	2.86	4.20	8.50	12.00	16.62	17.96*
	0.040	1.25	5.90	0.43	3.20	4.00	9.00	10.90	16.76	17.50

* Cementing agent that was stood 2 days for neutralization with sulphuric acid.

noted parameters of the cementing agent output from the first furnace. In should be emphasized that the cementing agent after the second reaction furnace possesses more homogeneous physicochemical properties as distinct from the cementing agent after the first furnace. The dispersion of W/S ratio values, of cementation time, and of the breakup point of the cementing agent obtained after the first and second furnaces was 6 and 4%, 44 and 35% (start of the cementation), 46 and 35% (finish of the cementation), 40 and 15% (the breakup point after 7 days of the solidification), 50 and 11% (the breakup point after 28 days of the solidification), respectively.

Thus the correction of the operation regime of the main equipment led to formation sufficiently homogeneous and stable composition of the FA with CaF_2 and H_2SO_4 amount in operation range of 3.0 and 7.0 wt %, respectively. Homogeneous composition of the FA enables obtaining the cementing agent with stable strength characteristics and sufficiently stable cementation time that allows its application in the cement manufacture both as a regulator and as a mineralizer in the dry pack manufacture. It should be noted that the strength characteristics of the cementing agent allow a partial substitution of the cement by them in some building products, and that the formation FA with more homogeneous and stable properties and composition occurs in the second furnace mainly with the help of the replacement of the gas-jet, thus the replacement of the gas-jet in the first furnace also is reasonable.

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