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Study of cryolite preparation from fluoride-containing acid slag in aluminium industry

TANG Wei-xue(唐维学)

(Guangzhou Research Institute of Non-ferrous Metals, Guamg zhou 510651, China)

Abstract: A new process of cryolite preparation is studied in this work by selecting a proper system of reaction and weeding impurity technology. The quality of artifial cryolite reaches and exceeds the first level of national standard. The utilization efficient of fluoride-containing acid slag is above 99.5%. It brings considerable economic benefit, and the environment is improved.

Key words: fluoride-containing acid slag; preparation; cryolite

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1 Introduction

Fluoride-containing acid slag made by acid corrosion process in aluminium industry is a kind of solid matter harming to people, because the fluoride in it can be dissolved by water. The existing treatment ways of landfilling lead to long-term pollution for the environment, at the same time, it is huge waste for abandoning high-content fluoride and aluminium of acid slag. So a technological process to deal with fluoride-containing acid slag is studied in this paper. The steps are following: weeding-impurity→conversion synthesis→precipitate filtration→drying→packing. The quick analysis and quality control for intermediate products show that the quality of product can be guaranteed in spite of the character of raw material is variable. We change a kind of low-value industrial wastes into high-quality chemical products without secondary pollution, and the pollution of fluoride-containing acid slag is resolved.

2 The main components and modes of occurrence of fluoride-containing acid slag

Acid slag is whiter massive material by self-drying in the air. By X-ray diffraction(XRD) and chemical analysis, its modes of occurrence include: $(NH_4)_3AlF_6$, $(NH_4)_2AlF_5$, NH_4AlF_4, all of which, $(NH_4)_3AlF_6$ is up to 95%. Table 1 shows the main components.

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Biography: TANG Wei-xue(born in 1968), Male, Engineer, Master.

Table 1 The main components of acid slag (mass fraction, %)

Components	Content	Components	Content	Components	Content
F	35−45	H_2O	21−32	Pb	0.001−0.01
Al	8−15	CaO	0.1−1	Cu	0.001−0.01
K,Na	0.1−1	P_2O_5	0.1−0.5	Ni	0.001−0.01
SiO_2	0.1−1	SO_4^{2-}	0.1−1	Cr	0.001−0.01
Fe_2O_3	0.1−1	NH^{4+}	20−25	Mg	0.1−1

3 The chemical principle and process course of cryolite preparation by acid slag

3.1 The chemical principle

The main components of cryolite made by fluoride-containing acid slag are Na_3AlF_6. The reactions are following:

$$5AlF_6^{3-} + Al^{3+} \longrightarrow 6AlF_5^{2-} \quad (1)$$

$$2AlF_6^{3-} + AlF_3 \longrightarrow 3AlF_5^{2-} \quad (2)$$

$$(NH_4)_3AlF_6 + 3NaCl \longrightarrow Na_3AlF_6 + 3NH_4Cl \quad (3)$$

$$NH4F + (NH_4)_2AlF_5 + 3NaCl \longrightarrow Na_3AlF_6 + 3NH_4Cl \quad (4)$$

3.2 The process course

weeding-impurity→conversion synthesis→precipitate filtration→drying→packing

4 Results and dicussion

Reaction temperature, acidity and usage of sodium chloride are studied in the experiment.

4.1 Impacts of temperature on rate of reaction and yields of products

Complex drug for weeding-impurity is added to acid slag (150g), then adjusts pH value of the solution, the impurities in acid slag, such as Si, Fe, P, Ca, Mg and SO_4^{2-} will be reduced and them meeted to needs of products. According to stoichiometric calculate, 400 mL saturated sodium chloride solution and 30 mL saturated alunimium chloride solution are mixed and reacted. The final products is calculated in the form of NaF : AlF = 3 : 1. Examing: the impacts of temperature on rate of reaction (macroscopic analysis). The statistical results after twenty experiments are following.

Table 2 shows that with the rise of reaction temperature, the rate of reaction quickens.

Table 2 The impacts of temperature on rate of reaction

Temperature /℃	Conversion ratio/%	Time /min	Temperature /℃	Conversion ratio/%	Time /min	Temperature /℃	Conversion ratio/%	Time /min
10	95	360	30	95	180	45	95	100
20	95	240	35	95	160	50	95	80
25	95	210	40	95	130	60	95	30

Table 3 shows that with the rise of reaction temperature, moisture and ignition loss of products increase. When temperature exceeds 40℃, the moisture of products is above the first level of national standard (0.5%), and ignition loss is above 3.0%. The rise of reaction temperature makes yields of products decreasing, which may have relation to the solubility of products. Because the solubility of products increases with the rise of temperature.

From Table 2 and Table 3, we can see: the optimal reacion temperature is 20—35℃. Room temperature can be selected in industrialization production.

Table 3 The impacts of temperature on yields of products

Temperature /℃	Moisture /%	Ignition loss/%	Yields /g	Temperature /℃	Moisture /%	Ignition loss/%	Yields /g	Temperature /℃	Moisture /%	Ignition loss/%	Yields /g
10	0.10	2.0	101	30	0.24	2.3	100	45	0.63	3.6	90
20	0.15	2.0	100	35	0.40	2.7	98	50	0.85	4.3	85
25	0.21	2.1	100	40	0.51	3.1	95	60	1.1	5.5	70

4.2 Impacts of acidity on quality of products

Complex drug weeding-impurity is added to acid slag (150g), then adjusts the acidity of the solution at the temperature of 25℃, the statistical results after twenty experiments are following:

Table 4 shows that: with the rise of acidity, moisture and ignition loss of products increase. When pH value less than 4.5, the moisture of products is above the first level of national standard (0.5%), and ignition loss is above 3.0%. When pH value is above 6.5, P_2O_5 is above the first level of national standard (3.0%), and Fe_2O_3 is above the first level of national standard (0.08%). So the optimal pH value we selected is 4.5—6.0 in this experiment.

Table 4 The impacts of acidity on quality of products

Acidity (pH)	Moisture /%	Ignition loss%	Yields /g	$w(Fe_2O_3)$ /%	$w(P_2O_5)$ /%	Acidity (pH)	Moisture /%	Ignition loss%	Yields /g	$w(Fe_2O_3)$ /%	$w(P_2O_5)$ /%
3.5	0.68	4.5	98.0	0.050	0.020	6.0	0.30	2.0	100	0.065	0.028
4.0	0.53	3.8	99.1	0.050	0.022	6.5	0.28	1.8	100.1	0.070	0.030
4.5	0.50	3.0	99.6	0.050	0.023	7.0	0.20	1.5	100.5	0.08	0.035
5.0	0.45	2.8	100	0.055	0.025	8.0	0.15	1.0	100.5	0.085	0.050
5.5	0.35	2.1	100.1	0.060	0.027	9.0	0.10	0.7	101	0.090	0.085

4.3 Impacts of usage of sodium chloride on yields of products

In this experiment acid slag (150g), temperature 25℃, pH 5.5, then adjusts the usage of sodium chloride, the statistical results after twenty experiments are following:

The Table 5 shows that the ignition loss of products increases when saturated sodium chloride solution is deficiency. The reason is that $(NH_4)_3AlF_6$ can not fully translate Na_3AlF_6 or Na_2AlF_5. A mass of $(NH_4)_3AlF_6$ in the products is decomposed into NH4F and AlF_3. When the usage of saturated sodium chloride solution is above 400 ml, the yields of products is not variable.

Table 5 The impacts of usage of sodium chloride on yields of products

NaCl Solution/mL	Ignition loss/%	Yields/g	NaCl Solution/mL	Ignition loss/%	Yields/g
275	10	88	400	2.5	100
300	6.0	90	425	2.40	100.1
325	4.5	93.1	450	2.30	100.2
350	3.5	95.3	475	2.20	100
375	3.0	98.1	500	2.15	100.5

The laboratory experiment and magnifying experiment in industry are examined simultaneously, Fallaly, the conditions of industrial cryolite preparation are following: room temperature; pH 4.5—6.0; the weight ratio of acid slag and sodium chloride, (1.20—1.25) : 1.

5 The qulity of products

The detection results from our laboratory and South-China Products Quality Supervision & Inspection Center for China Non-ferrous metals industry are shown in Tables 6 and 7.

Table 6 The detection results of our laboratory (mass fraction, %)

Components									Ignition loss/%
F	Al	Na	SiO_2	Fe_2O_3	H_2O	CaO	P_2O_5	SO_4^{2-}	
54.1	13.2	27.2	0.26	0.066	0.42	0.12	0.024	0.86	2.0
55.2	13.5	28.3	0.30	0.070	0.40	0.11	0.030	0.90	2.3
53.9	13.3	27.1	0.20	0.055	0.38	0.10	0.029	1.00	2.2
54.8	13.0	26.5	0.21	0.045	0.39	0.11	0.028	0.95	2.0
53.2	12.9	27.0	0.23	0.050	0.41	0.13	0.027	0.98	2.7
54.2	13.1	28.1	0.25	0.060	0.43	0.12	0.026	0.70	2.8
55.0	13.8	29.0	0.24	0.061	0.40	0.11	0.025	0.83	2.4
56.0	14.0	26.5	0.26	0.063	0.48	0.10	0.020	0.92	2.2

Note: 1) Ignition at 550℃ for 30 min.

Table 7 The detection results of South-China Products Quality Supervision & InspectionCenter for China Non-ferrous Metals Industry (mass fraction, %)

	Components									Ignition loss[1]/%
	F	Al	Na	SiO_2	Fe_2O_3	H_2O	CaO	P_2O_5	SO_4^{2-}	
Measured volue/%	54.4	13.9	27.4	0.24	0.06	0.41	0.10	0.02	0.89	2.83
The first level of national standard	≥53	≥13	≤32	≤0.36	≤0.08	≤0.50	≤0.15	≤0.030	≤1.2	≤3.0

Note: 1) Ignition at 550℃ for 30min.

According to Tables 6 and 7, the quality of artificial cryolite reaches and exceeds the first level of national standard in this production process.

6 Conclusions

(1) It is proved that this production technology is feasible through the production practices of two

years.

(2) This production technology makes the chemical products of the high grade with the industrial wastes of low value without second pollution, turning waste into wealth, and solving the pollution problem of containing-fluorine acid slag.

(3) In this production process with simple equipment and small investment, and the process conditions are easy to control, so it is easy to be poputarized.

References

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