FORMATION AND SOLUBILITY OF POTASSIUM ALUMINOSILICATE①

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ABSTRACT The formation and solubility of potassium aluminosilicate were studied. At low temperatures, potassium aluminosilicate, which in general is amorphous, can be easily crystallized in saturated aluminate solution, and the structure may be stratum or frame; its solubility depends on the concentration of caustic soda and temperature. The results indicated that low concentration of K_2O in aluminate solution has little effect on the current industrial alumina production.

Key words potassium aluminosilicate structure solubility

1 INTRODUCTION

As we know, there exist certain amount of potassium hydroxides in the cyclic aluminate solution of the alumina industry. In general, man-made zeolite of potassium is crystallized more slowly than zeolite of sodium, and its ability to form additive salt in the same solution is weaker[1]. In China, most of bauxite is diaspore, which needs high temperature (more than 230 ℃) to be digested. When the diaspore is digested in the leaching process, the illite (the main potassium mineral) can also be reacted completely, so potassium hydroxide may be accumulated in the aluminate solution. When we experimented with Gejiu nepheline, we noticed that there was white sediment, which is different from sodium aluminosilicate, and that white sediment appears again in solution when we treated high silicon bauxite with pure potassium hydroxide solution. We then named this sediment "potassium aluminosilicate" to distinguish from man-made zeolite of potassium. The present work studies its formation, structure and solubility.

2 EXPERIMENTAL

The main component of high silicon bauxite is Al_2O_3 65.80%, SiO_2 13.82%, Fe_2O_3 5.1%, scorching reduction 14.29% (mass fraction). The solution of potassium hydroxide and potassium aluminate were made of chemically pure potassium hydroxide and aluminium hydroxide. Bauxite was digested for 2h at 105 ℃. After being filtered while hot, the filtrate was transferred into a stainless steel cup quickly, and frozen in open air. When the potassium aluminosilicate was crystallized entirely, filtered again and the product —a kind of white sediments was obtained. The experiment of solubility was carried out in a constant temperature thermostat by dissolving the white sediment gradually to equilibrium. SiO_2 was detected by colorimetric analysis of blue-molybdenum.

3 RESULTS AND DISCUSSION

The potassium aluminosilicate was obtained from two kinds of solutions which can react with

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high silicon bauxite. The mole ratio of the sediments and the concentration of the two solutions were as follows.

(1) Pure potassium hydrogen solution: K_2O 396.7 g/L (equal to Na_2O 261.6 g/L)

K_2O∶ Al_2O_3∶ SiO_2 = 1∶ 1.221∶ 2.538

(2) Potassium aluminate solution: K_2O 396.7 g/L, Al_2O_3 11.7 g/L

K_2O∶ Al_2O_3∶ SiO_2 = 1∶ 1.199∶ 2.728

The molar ratio of Al_2O_3∶ SiO_2 is 1∶ 1.68 in sodium aluminosilicate, but the molar ratio of Al_2O_3∶ SiO_2 in potassium aluminosilicate is less, i. e. the amount of SiO_2 in potassium aluminosilicate is greater.

When the sediment was heated in the solution, the potassium aluminosilicate was dissolved; when the solution was cooled, potassium aluminosilicate can be easily crystallized again in the saturated aluminate solution, but it was hardly crystallized well. If we added sodium silicate into potassium aluminate solution, it was very difficult to crystallize at room temperature, due to the activity of reaction point and temperature. According to X-ray diffraction analysis potassium aluminosilicate is an amorphous substance .

3.1 Thermomechanical analysis

Assuming the chemical formula of potassium aluminosilicate is $K_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and the sodium alumino-silicate is $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$ (n is confined as 2); since the thermodynamic data of the two kinds of aluminosilicate salt above are scarce, it can be calculated by considering a complex oxide substance made of two or more kinds of simple oxide substances, for example,

$$M_mO + YO_n = M_mYO_{n+1}$$

and the free energy of M_mYO_{m+1} can be calculated as follows:

$$\Delta G_f^{\ominus} = \Delta G_{f M_mO}^{\ominus} + \Delta G_{f YO_n}^{\ominus} + \Delta G_R^{\ominus}$$

The method and some basic thermodynamic data of the simple oxide substance can be looked up in Ref. [2, 3]. The results that $\Delta G_f^{\ominus}$ of sodium aluminosilicate is − 3952.85 kJ/mol and of potassium alumoinosilicate − 4367.80 kJ/mol were obtained by this method.

Obviously, under standard condition, potassium aluminosilicate is a stable compound.

3.2 Structure analysis[4]

The IR spectrum of the two kinds of potassium aluminosilicte is shown in Fig. 1. It indicates that the component of the initial solution has little effect on the structure of potassium aluminosilicate under condition of the experiment. Since high valence of aluminium and silicon can bond other atoms(including themselves) through sp^3 hybridized orbital, the structure of aluminosilicate is complicate, but silicate and aluminate anion can form into a series of alumino-silicate anions, which fit to a suitable cation[5], so their IR spectrum is similiar in the aluminate solution. In Fig. 1, 3 418, 1 641 cm^{-1} are the characteristic absorption peaks of crystallizing water; 992 cm^{-1} strong peak is Si-O peak by bond stretching vibration, and the peak is sharp, this explains that the polymerization degree of silicon is high, and the structure may be stratum or frame; 709 cm^{-1} weak peak belongs to Si-O-Si(Al) by bond curving vibration; 443 cm^{-1} is generally considered as Si-O characteristic peak in Si-O-Al bond.

The TGA showed that the crystallized water is lost at 525.0 ℃, which is similiar to the sodium aluminosilicate.

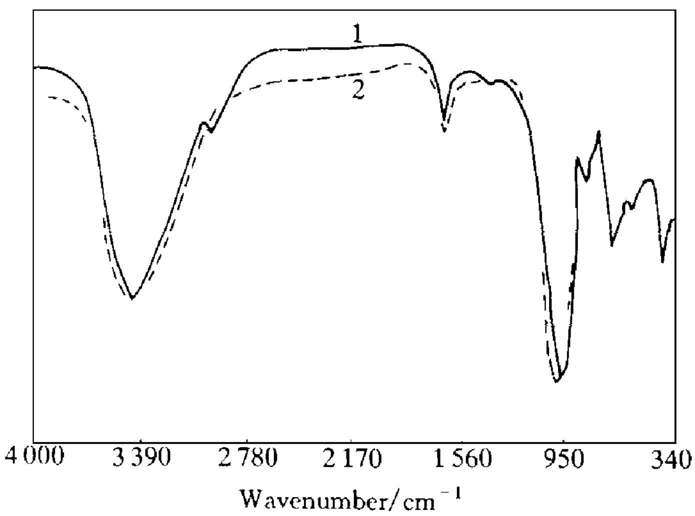

Fig. 1 IR spectrum of potassium aluminosilicate

1 —obtained from pure KOH solution;
2 —obtained from potassium aluminate solution

3.3 Solubility The solubility of sodium aluminosilicate in aluminate solution relates not only to the concentration of caustic soda, but also to the concentration of aluminium hydroxide. The reason is that there are aluminate and silicate anion in aluminate solution which are similiar in chemical character, so they can be condensed into a series of complex anion; another reason is that the substable concentration of SiO_2 is much higher than its equilibrium concentration. SiO_2 can be removed by adding seeds, reinforcing agitation or diluting solution.

The solubility of potassium aluminosilicate at different concentrations of caustic soda is shown in Fig. 2, which indicates that its solubility increases with the increase of concentration of caustic soda.

The solubility of potassium aluminosilicate at different temperatures is shown in Fig. 3, which indicates that its solubility increases with the temperature rise, owing to the fact that temperature rise leads to the formation of aluminosilicate anion[6].

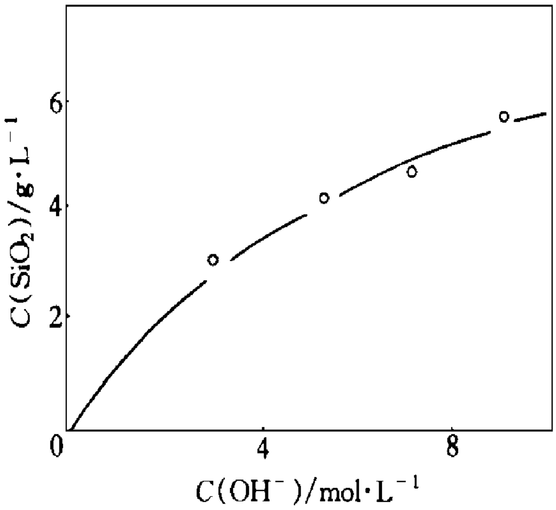

Fig. 2 Solubility of potassium aluminosilicate at different concentrations of caustic soda (80 ℃)

The experimental results indicated that the equilibrium concentration of SiO_2 in the potassium aluminosilicate is higher than that in sodium aluminosilicate in the caustic solution. Because the concentration of SiO_2 is low in the current aluminate solution, the current low concentration of K_2O has little effect on the alumina industry. But if the amount of potassium hydroxide is great, it will have obvious effects on the concentration of SiO_2, and the concentration of SiO_2 may rise up to several grams per liter.

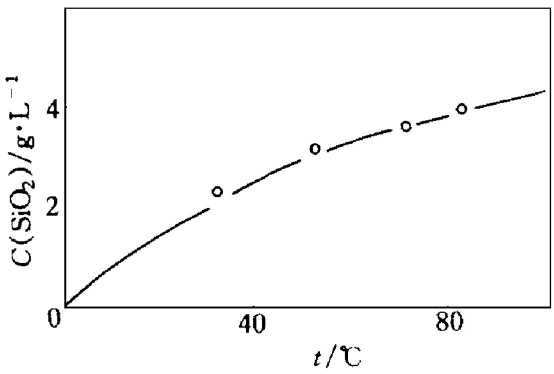

Fig. 3 Solubility of potassium aluminosilicate at different temperatures ($[OH^-] = 4.7$ mol/L)

4 CONCLUSIONS

(1) At low temperature, potassium aluminosilicate can be crystallized easily in saturate solution, its chemical formula can be expressed as $K_2O \cdot Al_2O_3 \cdot mSiO_2 \cdot nH_2O$ ($m \geqslant 2$), and the structure may be stratum or frame.

(2) The solubility of potassium aluminosilicate relates to the concentration of caustic soda and temperature. Under current industrial condition, low concentration of K_2O has little effect on the alumina production.

REFERENCES

1 Yang Zhongyu. The Production of Alumina, (in Chinese). Beijing: Metallurgical Industry Press, 1993: 256.

2 Wen Yuankai, Shao Jun *et al*. Geology Science(Ch), 1978, 4: 348.

3 Булах А Г ed., Xia Linxing transl. Thermodynamic Method of Mineral. Beijing: Geography Press, 1982: 136.

4 Wen Lu. IR Spectroscopy of Mineral, (in Chinese). Chongqing: Press of Chongqing University, 1988: 46.

5 Mortlock R F, Bell A T *et al*. J Phys Chem, 1991, 95(20): 2847.

6 Мюнб Л А, Сизяков В М. Ж П Х, 1995, 12: 1964.

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