PREPARATION OF LOW COST HIGH PURITY POTASSIUM FLUOROSILICATE FROM FLOUROSILICIC ACID PRODUCED IN IRAQI PHOSPHATE FERTILIZER PLANT

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ABSTRACT

The preparation of potassium fluorosilicate (K_2SiF_6) from fluorosilicic acid as an inexpensive by-product of Iraqi phosphate fertilizer plant has been investigated. The effect of molar ratio (KCl/H_2SiF_6), temperature and agitation on the purity and conversion were studied. The reaction was performed at different temperatures(25-60 ºC) for 1 hr under stirring, the precipitated material was separated from reaction mixture by filtration and dried under vacuum at$1*10^{-1}$ bar and 150 ºC. The results indicate that using higher molar ratio led to obtain a gelatinous form of K_2SiF_6 which is difficult to separate from reaction solution .Using higher reaction temperature was permitted to use higher molar ratio and getting high purity filterable product with higher conversion. Agitation was improved the conversion due to increase the crystal growth rate of K_2SiF_6. High purity of potassium fluorosilicate (99.25%) with a maximum conversion(71.04%) was obtained by using molar ratio(1.4),Temperature(60 ºC) ,and agitation(600rpm).The level of essential impurities (Cu ,Fe ,Ni)in the preparative material is lower than 0.05% which makes this material more suitable for using as raw material for silicon preparation by electro deposition method.

KEYWORDS: Potassium, F luorosilicate, Fluorosilicic Acid, Silicon, Phosphate Fertilizer.

تحضير مادة فلوروسليكات البوتاسيوم بنقاوة عاليه وكلفه واطئه من حامض الفلوروسيليسك المنتج عرضيا في مصانع الاسمده العراقية

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ألخلاصه

تم تحضير مادة فلوروسيليكات البوتاسيوم من حامض الفلوروسيليسيك المنتج في مصانع الاسمده الفوسفاتية العراقية.تم دراسة تأثير النسبة المولية (KCl/H_2SiF_6)،درجة الحرارة والخلط على كل من نقاوة المنتج ونسبة التحول.تم إجراء التفاعل بدرجات حرارة مابين (25-60 ºC)لمدة ساعة كاملة مع الخلط المستمر بعد ذلك تم فصل المادة المترسبة من خليط التفاعل بالترشيح وتجفيفها تحت ضغط مخلخل $1*10^{-1}$ bar بدرجة حراره 150 ºC. تشير النتائج إلى إن استخدام النسب المولية العالية يؤدي إلى الحصول على منتج هلامي يصعب فصله بينما استخدام درجات حرارية عاليه للتفاعل يسمح باستخدام نسب موليه عاليه مع الحصول على منتج عالي النقاوة ممكن فصله من خليط التفاعل بنسبة تحول اعلى. إن زيادة سرعة الخلط

أدى إلى زيادة نسبة التحول نتيجة لزيادة معدل النمو البلوري لفلوروسيليكات البوتاسيوم. تم الحصول على فلوروسيليكات البوتاسيوم بنقاوة((99.25%)وبنسبة تحول (71.04%)عند استخدام نسبه موليه(1.4) ، درجة حرارة(60 ºC) وسرعة خلط (600rpm) كأفضل ظروف تشغيلية. ان مستوى الشوائب الاساسيه (Cu ,Fe ,Ni) في المادة المحضرة كان دون مستوى(0.05%) مما يتيح استخدامها كمادة أوليه في تحضير السليكون بالطريقة الكهروكيميائيه.

INTRODUCTION

Potassium fluorosilicate (K_2SiF_6) is one of the most important materials in industry. It can be used as antiseptic of wood, assistant reagent in magnesium and aluminum smelted insecticide in agriculture, intermediate in organic synthesis, chemical reagent in analytical chemistry. Also used in antisepsis material, porcelain enamel, high quality welding rod production and mica synthesis (**Kirk-Othmer, 1991**). One of the most applications of Potassium fluorosilicate is in silicones industry. The thermal decomposition of potassium fluorosilicate in a fluidized bed reactor at 400 ºC gives Silicon tetra fluoride(SiF_4) which is a versatile gas that may be used as a precursor in the production of silane **(Bhusarapu,2010**).

In recent years there has been considerable interest to use Potassium fluorosilicate as a raw material for silicon electro deposition from solution of K_2SiF_6 in the binary LiF/KF or the ternary LiF /NaF/KF (Flinak) eutectics.This method is considered as an inexpensive method for producing elemental silicon because the ability of preparing 99% pure K_2SiF_6 from fluorosilicic acid, an inexpensive by – product of phosphate fertilizer production, and it has been demonstrated that inclusion free silicon films of high purity could be deposited from these solutions(**Gribov,2003&Elwell,1988**). In light of this, preparation of K_2SiF_6 at low cost would be a very promising approach to reduce the material processing cost for silicon prepared by this method.

Fluorosilicic acid is produced as a co-product in the manufacture of wet-process phosphoric acid and other phosphate fertilizers. The raw material, phosphate rock, contains fluoride and silica and is treated with sulfuric acid, which evolves the gases silicon tetra fluoride (SiF_4) and hydrogen fluoride (HF). These gases are passed through scrubbers and react with water to form fluorosilicic acid. The concentration and level of impurities of the produced acid depends entirely on the nature and properties of phosphate rocks used in this industry; however concentration of fluorosilicic acid prepared in this industry is not higher than 25% (**Kirk-Othmer, 1991b**).

Potassium fluorosilicates can also be produced by the reaction of silica with alkali and alkaline-earth fluoride bathes at 1000-1100 ºC (**Hitachi, 1983**). Although this approach gives higher purity of K_2SiF_6 ,but the energy consumed is too high in comparison with fluorosilicic acid approach. The preparation of Potassium fluorosilicate by neutralizing fluorosilicic acid is achieved either by using base or salts of potassium (**Sidun, 1958**). The reaction of acid with potassium hydroxide gives water as by-product (equation 1):

$$H_2SiF_6 + 2KOH \longrightarrow K_2SiF_6 + 2H_2O \quad (1)$$

While its reaction with potassium fluoride gives hydrofluoric acid as by-product which is highly corrosive material (equation 2):

$$H_2SiF_6 + 2KF \longrightarrow K_2SiF_6 + 2HF \quad (2)$$

The reaction of dilute acid with potassium chloride gives hydrochloric acid instead of hydrofluoric acid (equation 3):

$$H_2SiF_6 + 2KCl \longrightarrow K_2SiF_6 + 2HCl \quad (3)$$

Other compounds such as potassium sulfate, potassium nitrate, potassium bromide, potassium iodide, potassium acid carbonate and potassium acid sulfate can be used. But the availability and low cost of potassium chloride make it more suitable for the preparation potassium fluorosilicate. The molar ratio of the reactants, temperature and agitation are the main parameters influenced on the specifications of potassium fluorosilicate. The literatures indicate that 99% pure K_2SiF_6 can be produced cheaply from fluorosilicic acid (**Sidun, 1958&Coldwell, 1951**).

The aim of present research is to prepare high purity low cost potassium fluorosilicate from fluorosilicic acid (H_2SiF_6) produced in Iraqi Fertilizer plants. The effects of molar ratio (KCl/H_2SiF_6), temperature, and agitation on the conversion and purity of potassium fluorosilicate are investigated.

EXPERIMENTAL WORK

Materials and Equipments

Fluorosilicic acid solution was obtained from Iraqi phosphate fertilizer plant in "UKASHAT" location. It was analyzed and found that the concentration of fluorosilicic acid is (220g/l), and the level of impurities is shown in **Table 1.**

Fluka potassium chloride (99.5%), Preston Ltd. and deionized water were used in all the experiments. A Pyrex round bottle flask (1L) with three necks was used as a reaction vessel, the heating was carried out using heating mental (Type: HUMANLAB, Model: MS-DM-604) .A variable speed electrical agitator (type: SIEHE, No. SJB-S 450) provided with two blade glass rode was used for achieving the mixing at different speeds .The filtration was accomplished by using puchner filter (1L) under vacuum .A vacuum oven (Type:LINBERG, Model:VO1218A,Vloume:50L,Vacuum $1*10^{-1}$ bar, Temp. up to 260 ºC) was used to dry the prepared material .**Figure 1** shows the schematic diagram of laboratory system. The chemical and physical analyses of the samples were achieved using atomic absorption technique (SHEMADZO-2100) and particle size analyzer –laser B (FRITSCH, Type: 22-902, No.212). In IBN SINA state company, Iraq, while Scanning electron microscopy (SEM) analysis was performed on a Carl Zeiss EVO-40 fitted with backscatter detector in the laboratories of Cardiff University–School of Chemistry - Wales - Great Britain.

PROCEDURE

Before each run was done, fluorosilicic acid solution was filtered to remove any suspended solid impurities .KCl solution was prepared by dissolving the required amount of potassium chloride in 250ml dionized water, the resulting solution was filtered and stored in volumetric flask (250ml). In each experiment, 250ml of fluorosilicic acid was put into round bottle flask (1L), heated to the desired temperature .Meanwhile KCl solution was heated to the same temperature then added gradually to fluorosilicic acid solution with continuous agitation. The reaction was carried out at different temperatures (25-60 ºC) for 1 hr. The mixture was allowed to cool and was then vacuum filtered using puchner filter connected with vacuum pump (**Leybold Model D2.5E**) equipped with two liquid traps. The solids recovered were rinsed with distilled water, dried in a vacuum oven at $1*10^{-1}$ bars and 150 ºC. Samples of prepared material were characterized for their purities and average particle size. Factorial experimental design was carried out at tow levels for three factors to investigate the effect of molar ratio, temperature and agitation on the purity and conversion as shown in **Table 2.**

RESULTS AND DISCUSSION

The effect of molar ratio on the purity and conversion was studied at 25 ºC and 200rpm. **Figures 2 and 3** show the effect of molar ratio (KCl/H_2SiF_6) on the conversion and purity of K_2SiF_6 .It was observed that higher molar ratio gives higher conversion and lower purity. On the other hand the prepared potassium fluorosilicate was difficult to separated by filtration and having a gelatinous form when the molar ratio is higher than 0.53. In this case the separating of the solid material was achieved by settling the solution for 24 hours in a separating funnel; the gelatinous part was separated and evaporated to the dryness.

From practical point view, it is recommended using molar ratio higher than (0.53) to obtain higher conversion since the conversion was very law per pass (19.35%) at this molar ratio. The increasing of conversion could be achieved either by treating the same solution of fluorosilicic acid with a twice amount of potassium chloride solution, or by increasing the temperature of reaction.

Additional experiment was done using duplicated amount of KCl at the same molar ratio (0.53), the results indicate a cumulative conversion up to 40% which still lower than industrial accepted value. The purity of resulted material was lower than 99%, therefore increasing reaction temperature should be adopted to increase the conversion. **Figures 4 and 5** illustrate the effect of temperature on the conversion, and the purity of potassium fluorosilicate. It has been found that temperatures exert an important influence upon the formation of crystalline potassium fluorosilicate. Increasing the temperature of reacting solutions above 30 ºC affords a means of enhancing the size of particles that formed with easy separation where higher molar ratio can be used (1.4) with higher conversion per pass (60%) at 60 ºC.

The use of relatively high reaction temperature was permitted the use of relatively more concentrated solution of potassium chloride with a substantially increasing in potassium fluorosilicate purity. In spite of conversion higher than 60% could be obtained at temperatures higher than 60 ºC ,it is not recommended using temperature higher than 60 ºC because of high evaporation rate of solution occurred and evolving HCl gas at increasing rate.

The effect of agitation on the purity, conversion and particle size of potassium fluorosilicate is shown in **Table 3.** It was found that agitation improved the conversion with a slightly increase in purity. The average particle size increased with increasing the agitation. This effect may be interrupted as increasing of crystals growth rate rather than nucleation rate due to increasing mass transfer in the reaction system.

According to above results, it was found that the preferred conditions for preparation potassium fluorosilicate are:-

- Molar ratio : 1.42
- Temperature : 60 ºC
- Agitation :600 rpm
- Potassium chloride concentration :160 g/l
- Fluorosilicic acid concentration :220g/l

Under these conditions higher yield (71.04%) with a filterable material was obtained at purity not less than 99.25%.The prepared material has bulk density (1.48 g/cm^3) and average particle size (73µm).The chemical analysis of the prepared material is shown in **Table 4.** According to Rao results (**Rao, 1981&1980**), the most important impurities should be considered in preparation of silicon from K_2SiF_6 are (Cu, Fe, Ni) with total concentration should not exceeded 0.1%. The result of present work indicates that total concentration of these impurities in the prepared material is lower than 0.05% which is a very promising step for using this material to prepare silicon for solar cell application.

Figure 6 shows the scanning electron micrograph of the prepared potassium fluorosilicate. The crystalline structure was granular including cubic or hexa square crystals and some of them tend to be semispherical. The semispherical structure may be resulted from the action of friction among particles of prepared material during the gradually cooling of reaction mixture under stirring.

CONCLUSIONS

Potassium fluorosilicate was obtained from H_2SiF_6 produced as a by–product in Iraqi phosphate fertilizer plant with purity about 99.25%.The molar ratio and temperature have the major effect on the successful operation of this material at a filterable form. The operation at 25 ºC limited the molar ratio to (0.53) while increasing the temperature to 60 ºC led to using higher molar ratio up to (1.4).Increasing the agitation improved the particle size and the conversion to an industrial acceptable conversion .The higher purity of prepared material makes it more suitable for using as a raw material in preparation of SiF_4 or Silicon.

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Table 1 Impurity Analysis of fluorosilisic acid

Element	AL	As	Fe	K	Cu	Na	Mg	Zn	Ni	Pb
Concentration.(ppm)	15	21	28	25	180	320	72	31	10	24

Table 2 Experimental Design (*Factorial*)

Factors	Low level(-1)	High level(+1)
Molar ratio (KCl/H_2SiF_6)	0.26	2.6
Temperature(ºC)	25	60
Agitation(rpm)	200	600

Table 3 . Effect of agitation on the conversion and purity of potassium fluorosilicate

Agitation* (rpm)	**Quantity of K_2SiF_6(g)**	**Conversion (%)**	**Purity (%)**	**Average particle size (µm)**
200	51.00	52.78	99.20	45
400	54.80	65.00	99.23	61
600	60.20	71.04	99.25	73

* fluorosilicic acid concentration(220g/l),mass(55g),volume(250ml),temperature (60 ºC), Potassium chloride concentration (160g/l),mass (40g),volume(250ml), KCl/H_2SiF_6(1.4).

Table 4 . Chemical Analysis of the prepared potassium fluorosilicate

Index name	Index	Index name	Index
Potassium fluorosilicate (K_2SiF_6), %	99.25	Mg ,%	0.005
Iron (Fe), %	0.02	Chloride (base on Cl), %	0.14
Zn, %	0.007	Cu, %	0.016
Pb, %	0.006	Ni,%	0.011
AL, %	0.02	As, %	0. 007

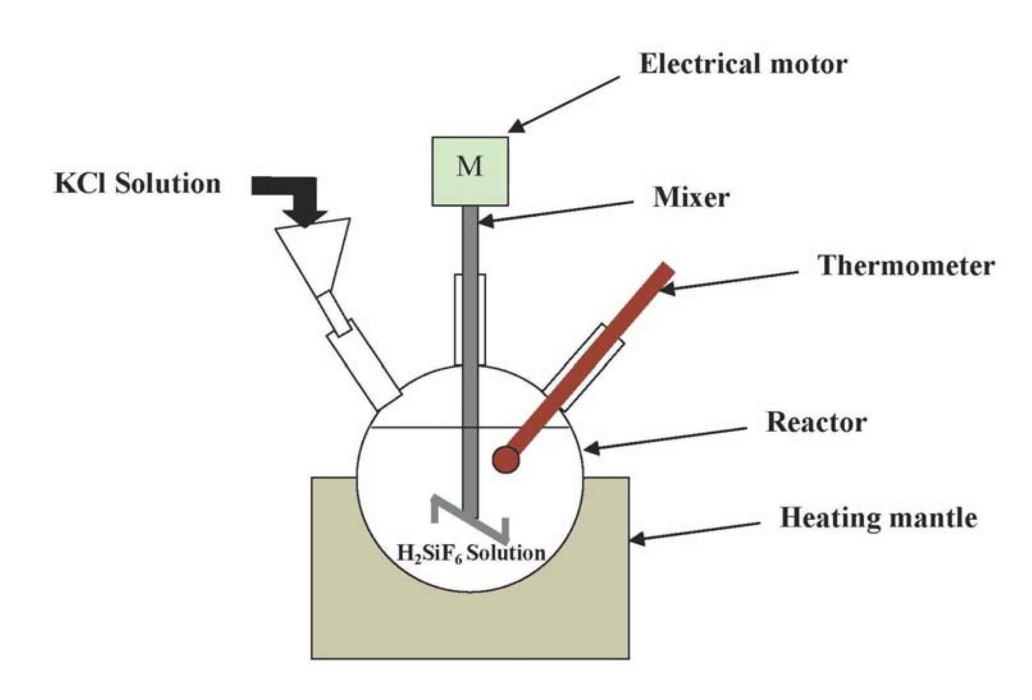

Figure 1 Schematic diagram of laboratory system

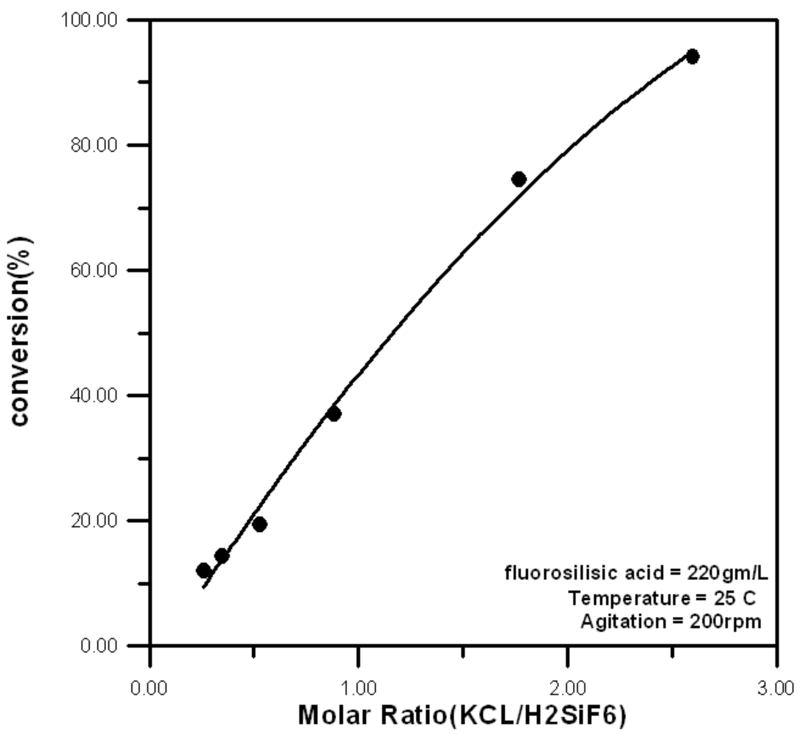

Figure 2 Effect of molar ratio on the conversion of H_2SiF_6

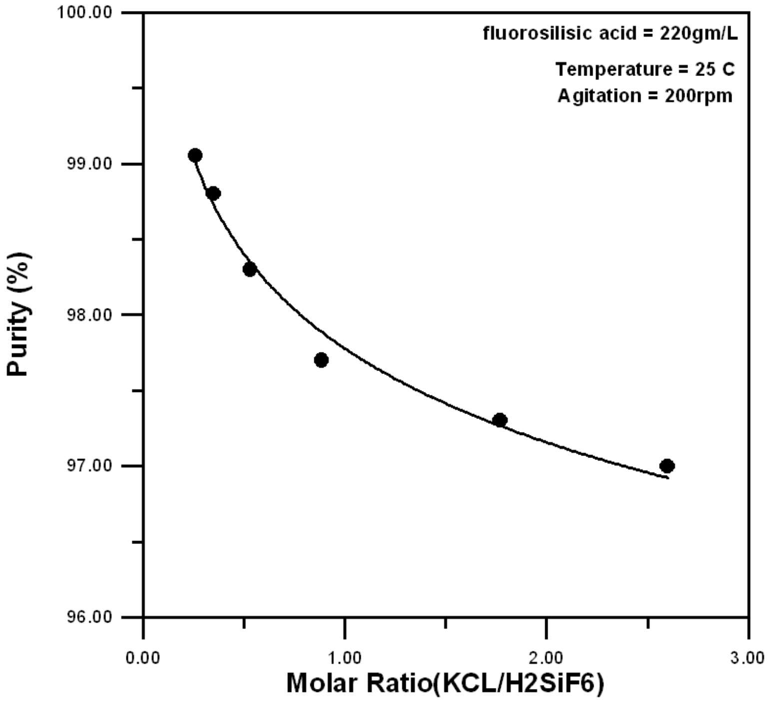

Figure 3 Effect of molar ratio on the purity of K_2SiF_6

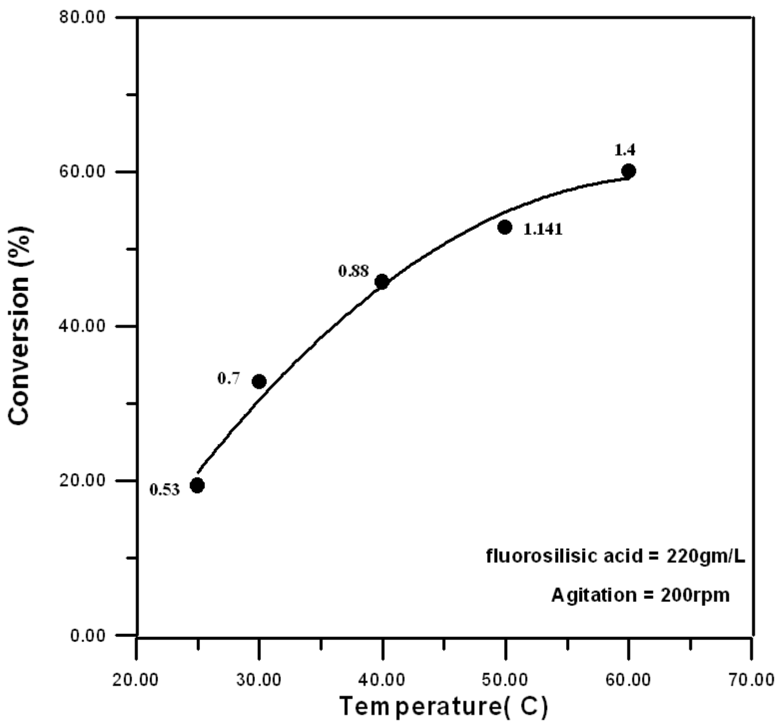

Figure 4 Effect of Temperature on the conversion of H_2SiF_6 numbers on the points refer to the molar ratio (KCl/H_2SiF_6)

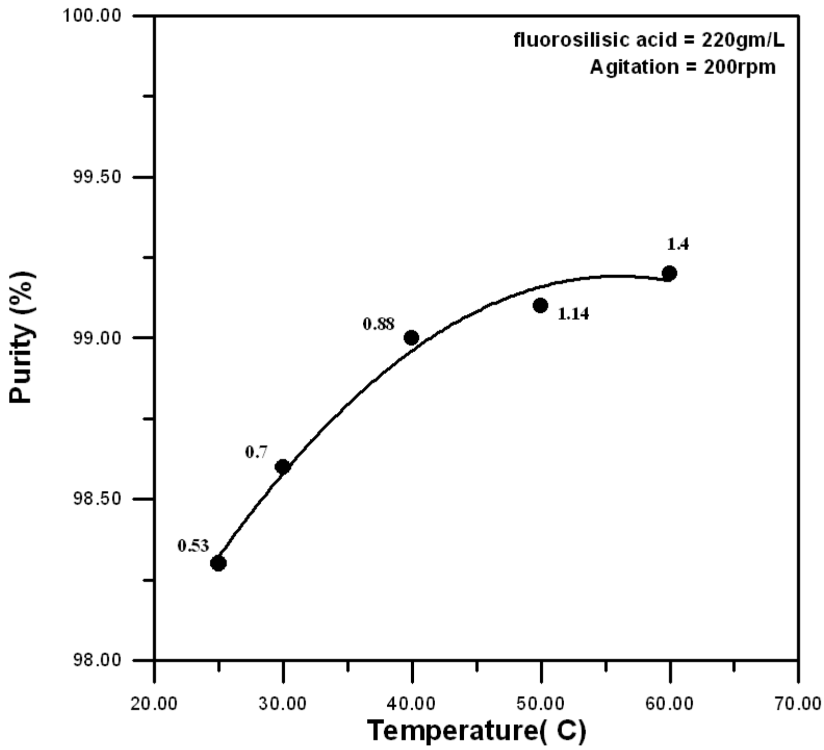

Figure 5 Effect of Temperature on the purity of K_2SiF_6 numbers on the points refer to the molar ratio (KCl/H_2SiF_6)

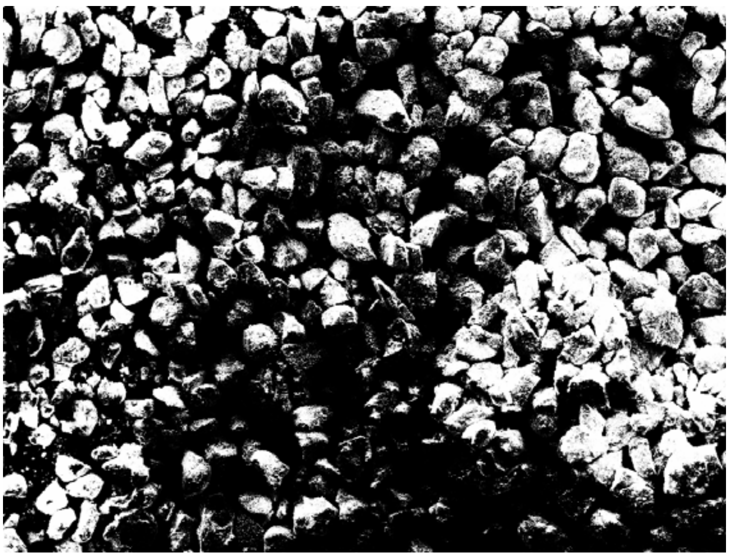

Figure 6 Scanning electron micrograph of the prepared potassium fluorosilicate (*EHT=20.00Kv, WD=9.0mm, Signal=SE1*)