

PRODUCTION OF CALCIUM FLUORIDE FROM CALCIUM CARBONATE

Dimitrios M. Arabadžiev, Trajče Stafilov, Viktor Stefov

*Institute of Chemistry, Faculty of Science, Sts. Cyril and Methodius University,
 P. O. Box 162, MK-1001 Skopje, Republic of Macedonia*

Abstract: An optimized procedure for production of calcium fluoride (CaF_2) based on a reaction of limestone (CaCO_3) with hexafluorosilicic acid (H_2SiF_6) is proposed. Silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) and carbon dioxide (CO_2) are obtained as secondary products of the process. The conditions for favorable and complete realization of this reaction which have been studied are the following: the required quality of the raw materials (limestone and hexafluorosilicic acid), the mass ratio between carbonate and water in the initial suspension, the concentration of hexafluorosilicic acid that is introduced into the suspension, the needed pH of the solution to complete the reaction, the time needed for adding the acid and for mixing the suspension, the method of separation of the products and their treatment, etc. Very high quality products are obtained using this procedure. The obtained calcium fluoride contains 94–97 % (*m/m*) CaF_2 , calculated for dry substance. The content of CaCO_3 is lower than 1 % and the content of SiO_2 is below 3 %. The yield of the secondary product silicic acid contain is also very high, from 92–96 % SiO_2 (calculated for dry substance).

Key words: calcium fluoride; production; limestone; hexafluorosilicic acid; silicic acid

INTRODUCTION

The utilization of calcium fluoride (CaF_2) and silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) in different areas of industry is very high. Their application is very much dependent on their purity, which has lately motivated a lot of researchers to work on developing procedures for obtaining these products by different methods.

From literature data different methods using various approaches in the synthesis of CaF_2 are available. Calcium fluoride is obtained in different ways: by reaction of CaCl_2 with gaseous HF (Hass and Kemnitz, 1979); by dilution of CaCO_3 in excess of HF (Fomin *et al.*, 1986); by reaction of CaSO_4 with NH_4F (Saiko *et al.*, 1992). CaF_2 can also be obtained by treatment of M_2SiF_6 (where $\text{M} = \text{Na}$ or K) with hydroxides of the same metals where the product is MF, which in reaction with $\text{Ca}(\text{OH})_2$ gives CaF_2 (Zelikin and Bakulina, 1957).

CaF_2 can be synthesized using reactions with ammonia or ammonia solutions, as well (Rodin *et al.*, 1978; Tumanov *et al.*, 1989).

The synthesis of CaF_2 can also be performed by adding H_2SiF_6 in a solution of $\text{Ca}(\text{OH})_2$ at tem-

peratures near the boiling temperature of the solution (Sidkar, 1981). A lot of procedures for obtaining CaF_2 by reaction of H_2SiF_6 with various reactants are available in literature (Volfkovich and Gabrielova, 1952; Tumanov *et al.*, 1989; Gabryel *et al.*, 1989; Gordeev, 1991; Babkin *et al.*, 1992; Stafilov *et al.*, 1997).

The main goal in developing new methods or improving the existing procedures for obtaining different products is to achieve products with higher quality using cheaper and simpler methods.

Starting with this assumption, in this work an original procedure is developed for manufacturing of calcium fluoride (CaF_2), silicon acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), and at the same time of carbon dioxide (CO_2). For this procedure cheap raw materials: limestone (calcium carbonate – CaCO_3), in which Republic of Macedonia is very reach and hexafluorosilicic acid (H_2SiF_6), which is also available. The results from this study enable introducing the proposed procedure with industrial dimensions in production of the cited products.

EXPERIMENTAL

All experiments were performed using CaCO_3 (p.a.) from Merck and granulometric content below $16 \mu\text{m}$ (100 %), and H_2SiF_6 (purum) from Fluka.

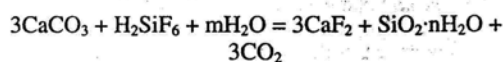
Here, it is important to point out that all vessels and instruments used in the laboratory work were made of plastic material or Teflon to prevent

the possible corrosion of metal and glass by H_2SiF_6 (probably because of the presence of HF).

The synthesized CaF_2 was analyzed by the standard GOST 7619.0-81 and the silicic acid by the standard GOST 4214-78.

RESULTS AND DISCUSSION

The basis of this process is the reaction between calcium carbonate (CaCO_3) and hexafluoro-silicic acid (H_2SiF_6):



The influence of many factors on the performance of this reaction aimed towards obtaining high quality products and complete realization of the reaction was studied. That is the reason for this thorough study for establishing the optimum values of all the relevant parameters involved in the reaction.

The procedure for synthesis of CaF_2 by reaction of CaCO_3 and H_2SiF_6 was based on introducing a solution of the acid in the reaction mixture composed of suspension of CaCO_3 in water. Many syntheses were performed in order to establish the optimum mass ratio of CaCO_3 and water in the suspension. The mass ratio was varied from 1:5 to 1:35, and the concentration of the added acid was varied in the range from 5 to 24 %. The results of these experiments show that the reaction is nearly completed (the obtained CaF_2 with CaCO_3 content below 1 %). As expected, when more diluted acid is added, it is necessary to add higher volumes of the solution in order to complete the reaction. As for the quality of the obtained CaF_2 (estimated by the content of SiO_2), best results were obtained when the reaction was performed using suspension with a mass ratio of CaCO_3 and water higher than 1:15. This can be attributed to the fact that the gel of silicic acid in more viscous suspensions can easier coprecipitate on the obtained product (CaF_2). On the other hand, suspensions with smaller content of water are favorable because of the energy needed for evaporation of the water from the filtrate, but in those cases the quality would not be the best.

The results of the investigations show that almost in the whole assayed concentration range of the acid (5-24 %) the reaction is completed and the quality of the products is satisfactory. Because of the needed little volume of the solution at the end of the reaction, higher concentration of the acid solution, which is added to the aqueous suspension of CaCO_3 , is preferred. The optimal concentration suggested for this procedure is 15 % of H_2SiF_6 .

The influence of the final pH-value at the end of the reaction on the quality of the obtained products was investigated, as well. For this investigation, syntheses with varying pH-values of the solution in the range from 1.5 to 7 were performed. In the cases with low pH-values, bigger volumes of the acid solution are added, which induces higher content of this acid in the obtained silicic acid. On the other hand, higher pH-values cause remains of CaCO_3 that have not been used in the reaction to become part of the product and to reduce its quality. The investigation for establishing the optimum pH-value showed that at pH-values below 2 the solubility of CaF_2 is higher, which causes loss of it during filtration (yield of CaF_2 lower than 80 %). In this case the content of CaCO_3 is 0 and the content of SiO_2 is less than 2 %. When increasing the pH-value, the yield of CaF_2 is higher, but the content of CaCO_3 and SiO_2 are higher, as well. At pH-values higher than 6.5 the content of CaCO_3 is higher than 1 % and the content of SiO_2 higher than 3 %. All these results bring to the conclusion that the optimum pH-value is in range between 2 and 6.5.

The time needed to add the acid solution and mix the suspension after adding the acid has a double influence on the process. For industrial use, the time needed to for the reaction mixture to remain in the reactor is very important because it controls the capacity of the production equipment. On the other hand, the duration of these steps de-

termines the quality of the products. For that reason the optimal duration of adding the acid solution was investigated using the previously established optimal mass ratio between CaCO_3 and water, acid concentration and pH-value of the solution. The time for adding the acid solution was varied from 0 to 60 minutes and, for every investigated duration of adding the acid, different period of mixing was employed, in the range from 0 to 60 minutes. The results show that the optimum period for adding the acid solution is longer than 30 minutes. Longer than 30 minutes duration of this step enables complete realization of the reaction and better quality of the obtained products, but it is not favorable from economic point of view. So the period of 30 minutes is suggested as the optimum time for adding the necessary quantity of acid. The results of the investigation show that the optimum duration of mixing must not be below 30 minutes. It is also important to mention that the way and the type of mixing has an influence on these periods. It is beneficial to have a mixer with high rotation speed.

The results of the investigation show that the temperature has no significant influence on the quality of the products when the reaction is performed in the temperature range between 15 and 35 °C.

As expected, a vital influence of the efficient filtration (separation) of CaF_2 from the solution of the diluted silicic acid on the quality of the obtained products was demonstrated. When the filtration is performed slowly, often the obtained CaF_2 is contaminated with SiO_2 . In some cases the content of SiO_2 in the CaF_2 was up to 10 %. That is why the filtration must be done with effective vacuum filters (like Nuch filters or Büchner filters) or the separation must be performed by centrifugation. In order to remove the possible adsorbed molecules or gel particles of silicic acid, it is necessary to wash the sediment of CaF_2 with water after filtration or centrifugation. The investigation showed that for effective washing, more than half of the quantity of water used for the suspension is needed for washing.

Very high quality products are obtained using this procedure. The obtained calcium fluoride contains 94–97 % (*m/m*) CaF_2 , calculated for dry substance. The content of CaCO_3 is lower than 1 % and the content of SiO_2 is below 3 %. The yield of the secondary product silicic acid contain is also very high, from 92–96 % SiO_2 (calculated for dry substance).

Acknowledgment. This work was financially supported by the Ministry of Science of the Republic of Macedonia, and this support is gratefully and sincerely appreciated.

REFERENCES

- Babkin, V. V., Koryakov, V. V., Dokolova, T. A., Petrova, N. K., 1992: Manufacture of calcium fluoride using carbonate raw material, *Khim. Prom-st.*, 163–4.
- Gabryel, H., Kacalski, L., Glabisz, U., 1989: Study of one-step calcium fluoride production from hexafluorosilicic acid, *Chem. Stosow.*, 33, 673–678.
- Gordeev, M. A., Kuznetsov, K. A., Pyatina, T. B., Zaitsev, V. A., 1991: Processing of fluorosilicic acid with production of calcium fluoride and silicon dioxide, *Khim. Prom-st.*, 340–4.
- GOST 7619.0–81
- GOST 4214–78.
- Fomin V. K., Varlamova N. I., Kozma V. P., Esin M.N., 1986: Calcium fluoride production, *SU Patent* 1 224 263.
- Hass, D., Kemnitz, E., 1979: Formation of calcium fluoride from gaseous hydrogen fluoride and solid calcium chloride, *Z. Anorg. Allg. Chem.*, 455, 99–102.
- Rodin V. I., Zaitsev V. A., Kuznetsov V. A., Rukhman B. E., Palesheva, T. S., 1978: Ammonia method for obtaining calcium fluoride from sodium hexafluorosilicate, *Fosfor-naya Prom-st.*, 31, 29–34
- Saiko, I. G., Perebeinos, A. A., Pupysheva, L. M., and Orel, N. A., 1992: Manufacture of calcium fluoride, *SU Patent* 1 708 762.
- Sidkar S. K., 1981: Preparation of calcium fluoride from fluorosilicic acid solutions, *US Patent* 4 264 563.
- Stafilov, T., Stefov, V., Arabadžiev, D., and Stjepović, B., 1997: Procedure for obtaining calcium fluoride, silicic acid carbon dioxide, *MK Patent* 900412/MKP C01F 11/22.
- Tumanov V. V., Rodin V. I., Zaitsev V. A., Belova L. P., Zyrina T. A., Sokolova T. A., 1989: Production of synthetic calcium fluoride from hydrofluorosilicic acid, *Khim. Prom-st.*, 668–71.
- Volfkovich, S. I., and Gabrielova, M. G., 1952: Calcium fluoride and hydrogen fluoride from fluorosilicic acid, *Zh. Prikl. Khim.*, 25, 345–9.
- Zelikin M. B., Bakulina A. J., 1957: Obtaining of calcium fluoride, *Trudy N.I. Instit. Osnovn. Khim.*, 10, 111–115.

Резиме

ДОБИВАЊЕ НА КАЛЦИУМФЛУОРИД ОД КАЛЦИУМКАРБОНАТ

Димитриос М. Арабаџиев, Трајче Стафилов, Виктор Стефов

*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“,
б. бр. 162, МК-1001 Скопје, Република Македонија***Клучни зборови:** калциум флуорид; силициумова киселина; производство; варовник;
хексафлуоросилициумова киселина

Предложена е постапка за синтеза на калциум флуорид (CaF_2) заснована на реакцијата на варовник (CaCO_3) со хексафлуоросилициумова киселина (H_2SiF_6). Како секундарни производи се добиваат силициумова киселина ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) и јаглероден диоксид (CO_2). Оптимирани се условите за оваа реакција: потребниот квалитет на суровините (варовник и хексафлуоросилициумова киселина), масениот однос помеѓу карбонатот и водата во почетната суспензија, концентрацијата на хексафлуоросилициумовата киселина, потреб-

ниот рН на растворот за реакцијата, времето на додавање на киселината и времето на мешање на суспензијата, начинот на издвојување на продуктите и нивниот третман итн. Се добива калциумфлуорид со висок квалитет со содржина од 94–97 % (m/m) CaF_2 (пресметан на сува суспензија). Содржината на CaCO_3 е мала и е под 1 %, а содржината на SiO_2 е под 3 %. Квалитетот на силициумовата киселина како секундарен продукт е исто така висок, од 92–96 % SiO_2 (пресметан на сува суспензија).