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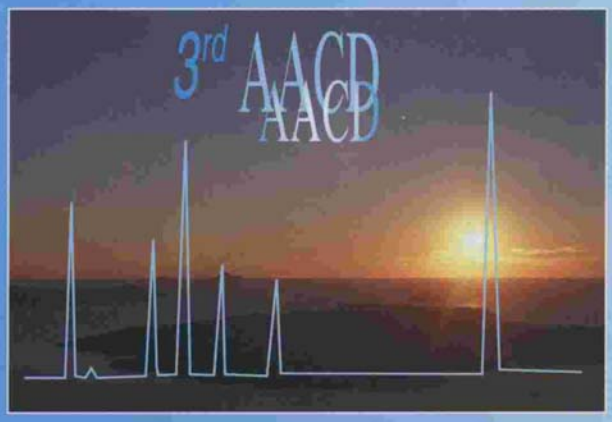

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INVESTIGATION OF THE PURITY OF SYNTHESIZED CALCIUM FLUORIDE BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AND GLOW DISCHARGE SPECTROMETRY

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Abstract

The utilization of calcium fluoride (CaF_2) in different areas of industry is very high. In this work an original procedure for production of calcium fluoride was developed using limestone ($CaCO_3$) and hexafluorosilicic acid (H_2SiF_6). The results from this study allow the development of a procedure for production of high quality calcium fluoride. The purity of the calcium fluoride obtained was tested by applying k_0-instrumental neutron activation analysis (k_0-INAA) and glow discharge spectrometry (GDS). The results show that the obtained product could be applied in the chemical industry for the production of various fluorine compounds and is a good starting material for the production of very high quality CaF_2 for the optical and other industries.

Introduction

The application of calcium fluoride is very much dependent on its purity, which has lately motivated many researchers to work on developing procedures for obtaining this product by different methods. From literature data different methods using various approaches in the synthesis of CaF_2 are available. Calcium fluoride may be obtained in different ways: by reaction of calcium salts with HF or NH_4F[1]. CaF_2 can also be obtained by treatment of M_2SiF_6 (where M = Na or K) with hydroxides of the same metals where the product is MF, which on reaction with $Ca(OH)_2$ gives CaF_2[2]. CaF_2 can also be synthesized using reactions with ammonia or ammonia solutions[3,4]. Some procedures for obtaining CaF_2 by reaction of H_2SiF_6 with various reactants are available in literature[5,6].

The main goal in developing new methods or improving existing procedures is to achieve products of higher quality using cheaper and simpler methods. Starting with this assumption, in this work an original procedure was developed for manufacturing calcium fluoride (CaF_2), silicon acid ($SiO_2 \cdot nH_2O$), and at the same time of carbon dioxide (CO_2). For this procedure cheap raw materials were used: limestone (calcium carbonate-$CaCO_3$), in which the Republic of Macedonia is very rich and hexafluorosilicic acid (H_2SiF_6), which is also available. The results from this study allow introduction of the proposed procedure on the industrial scale.

Experimental

k_0-Instrumental Neutron Activation Analysis

Aliquots of about 150 mg of sample were sealed in pure polyethylene ampoules (SPRONK system, Lexmond, The Netherlands). A sample and standard (Al-0.1%Au IRMM-530 disk of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 20 hours in the carousel facility of the TRIGA Mark II reactor of the Jožef Stefan Institute. After irradiation the sample and standard were transferred to clean 5 mL polyethylene mini scintillation vials for measurement. Each sample was measured twice on a calibrated HPGe detector[7,8], after 8-10 and 30 days cooling time. Measurements were performed as such distances that the dead time was kept below 10%. For peak area evaluation, the

* Editorial note: Recognized by Greece as FYROM

HYPERMET-PC[9,10] program was used. For elemental concentrations and effective solid angle calculations a software package called KAYZERO/SOLCOI®[11], operated on an IBM-compatible PC, was applied.

Glow Discharge Spectrometry

Glow discharge spectrometric analyses were performed on a Thermo Electron VG9000 System utilizing time-proven Glow Discharge Mass Spectrometry technology (GDMS). Samples were directly analysed as solid materials. Linear calibration plots and quantitative depth profile analysis were used to allow simple quantification at all concentrations. The Ion currents/ion counts collected during analysis for the selected isotopes are all ratio-ed to calcium internal standard (ion beam ratios). The ion beam ratios are then converted to element concentrations using relative sensitivity factors.

Results and Discussion

The basis of the process applied is the reaction between calcium carbonate ($CaCO_3$) and hexafluorosilicic acid (H_2SiF_6)[6]:

$$3CaCO_3 + H_2SiF_6 + mH_2O \rightarrow 3CaF_2 + SiO_2 \cdot nH_2O + 3CO_2$$

The influence of many factors on the performance of this reaction was studied with the aim of obtaining high quality products and completion of the reaction. For that reason a thorough study to establish the optimum values of all the relevant parameters involved in the reaction was carried out. 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 into the reaction mixture composed of a suspension of $CaCO_3$ in water. Many syntheses were performed in order to establish the main parameters: the mass ratio of $CaCO_3$ and water in the suspension, the concentration of the acid solution, the final pH-value at the end of the reaction, the time needed to add the acid solution and mix the suspension after adding the acid, temperature etc. After the optimization of these parameters high quality products were obtained. The calcium fluoride obtained contains 94-97% (*m/m*) CaF_2. 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 is also very high, from 95-98% SiO_2 (calculated for dry substance).

However, another process was applied for the further purification of the CaF_2 obtained[12]. The quality of two samples of highly pure calcium fluoride was checked by the application of neutron activation analysis and glow discharge spectrometry. Using these techniques the content of many trace elements was determined. The results obtained are given in Table 1. These data show that the CaF_2 obtained has a quality suitable for many applications. It was also found that the concentrations of many elements are very similar for those in high-quality CaF_2 crystals[13,14].

Table 1. Results obtained by k_0-INAA and GDS analyses of two samples of purified synthetic CaF_2. Contents are in mg/kg.

Element	Sample 1		Sample 2	
	GDS	k_0-INAA	GDS	k_0-INAA
Ag	<0.1	<0.05	<0.1	<0.04
Al	290		220	
As	1.6	3.35	2	3.40
Au	<5	<0.0005	<5	<0.001
B	2.6		1	
Ba	<0.1	3.79	<0.1	5.92
Be	0.01		0.02	
Bi	<0.05		<0.05	
Br	<0.5	1.10	<0.5	0.36

(continued)

Table 1 (continued)

Ca	Matrix	451000	Matrix	433000
Cd	<0.1	<0.3	<0.1	<0.3
Ce	0.66	1.02	0.5	0.87
Cl	26		23	
Co	<5	0.0061	<5	0.188
Cr	1.4	0.34	14	12.6
Cs	<0.1	<0.01	<0.1	<0.005
Cu	<1		<1	
Dy	0.11		0.14	
Er	0.11		0.1	
Eu	<0.05	0.029	<0.05	0.020
F	Matrix		Matrix	
Fe	79	103	140	212
Ga	<0.05		<0.05	
Gd	0.19	<0.3	0.1	<0.2
Ge	<0.1		<0.1	
Hf	<0.1	0.016	<0.1	0.013
Hg	<0.1	0.061	<0.1	0.038
Ho	<0.05		<0.05	
I	<0.1		<0.1	
In	<1	<0.1	<1	<0.1
Ir	<0.05		<0.05	
K	93		55	
La	<0.5	0.70	<0.5	0.62
Li	3.4		3.1	
Lu	<0.05		<0.05	
Mg	2500		2500	
Mn	3.3		3.4	
Mo	<0.5	<0.3	<1.5	<0.3
Na	460		450	
Nb	<2		<2	
Nd	0.26	0.51	0.46	0.52
Ni	<1		2.6	
Os	<0.01		<0.01	
P	92		90	
Pb	21		340	
Pd	<0.5		<0.5	
Pr	0.14		0.08	
Element	Sample 1		Sample 2	
	GDS	k_0-INAA	GDS	k_0-INAA
Pt	<0.1		<0.1	
Rb	<0.5	<0.4	<0.5	<0.3
Re	<0.05		<0.05	
Rh	<1		<1	
Ru	<0.1		<0.1	
S	49		380	
Sb	<0.5	0.072	<0.5	0.054
Sc	0.14	0.175	0.1	0.146
Se	<0.5	<0.08	<0.5	<0.06
Si	1700		1400	

(continued)

Table 1 (continued)

Sm	0.1	0.134	0.09	0.100
Sn	<0.5	<3	<0.5	<3
Sr	210	212	240	230
Ta	Binder	<0.005	Binder	<0.005
Tb	<0.05	0.023	<0.05	0.019
Te	<0.1	<0.1	<0.1	<0.1
Th	0.04	0.060	0.04	0.050
Ti	7.7		6	
Tl	<0.05		<0.05	
Tm	<0.05	0.023	<0.05	0.018
U	0.18	0.203	0.13	0.173
V	0.6		0.8	
W	<1	<2	<1	<2
Y	1.8		1.5	
Yb	0.06	0.094	0.12	0.080
Zn	<0.1	1.45	<0.1	1.31
Zr	0.62	<4	0.65	<1

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