POTASSIUM FELDSPARS WITH LOW IRON AND SODIUM CONTENTS FOR CERAMIC FRIT AND GLAZE PRODUCTION

D. Täfler; E. Colomer

AKWK Kick GmbH HIRSCHAU (Germany)
MOLTUVAL S.A., NULES (Spain)

ABSTRACT

This paper undertakes a geological, mineralogical and chemical study of the potassium feldspars of Hirschau, as well as their processing, physical properties and special applications in the tile industry, with regard to the elements that decisively impact final product quality. The vast industrial spectrum is considered in this respect, which today encompasses the manufacture of floor and wall tile, white stoneware, porcelain tile, frits and glazes, particularly highlighting the latter items. The study also describes the floatation reagents and processes that were researched, as well as the chemical analysis techniques used such as X-ray fluorescence, electrometric techniques, and X-ray diffraction, which have allowed preparing a highly advanced own technology, capable of producing these feldspars from the kaolin sands of Hirschau-Schnaittenbach. The results obtained are set out together with the conclusions that may be drawn.

The paper consists of the following sections: Introduction, Use of potassium feldspars low in iron and sodium; Deposits, Mineralogy and Chemistry: Processing; Physical characteristics and advantages of potassium feldspars from Hirschau.

1.0 INTRODUCTION: USE OF POTASSIUM FELDSPARS WITH A LOW IRON AND SODIUM CONTENT.

Feldspars are generally metal aluminosilicates, which may be alkalis or alkaline earths. The higher the atomic weight of the metal, the larger its percentage by weight in the silicate lattice. Thus for albite, the maximum percentage that may be contained is 11.8%, whereas for orthoclase (or orthose) this is 16.9%. This is of itself already an advantage. Both feldspars are usually found together in nature, in proportions ranging from 3:1 to 4:1 (orthoclase/albite). However, the potassium feldspars from Hirschau have an orthoclase/albite ratio of 13:1, with 0.03% Fe_2O_3 and 0.02% TiO_2, which provide it with important ceramic performance characteristics. The specific surface area of the feldspar grains also play their part (1).

Fast fire frits and clear glazes (crystalline frits) have been in use for fast single firing in Spain and Italy for several years now. These crystalline compositions are formulated with high percentages of potassium and aluminium (more than 8% K_2O with a similar amount of Al_2O_3, with hardly any Na_2O). This is technically possible by specifically using POTASSIUM FELDSPAR 900 SF, with evident savings in calcined alumina and potassium carbonate or nitrate. Potassium nitrate melts at 350°C, acting as a vigorous oxidant up to 400°C, but given the high melting temperature at which frits are obtained, and the oxide components (possible catalysts) that they contain, they must be used in minimum proportions. The most hazardous breakdown reaction (from an environmental point of view) is the one producing nitrogenous oxides (2), because of their effect on the ozone layer, as Paul Crutzen showed in 1972 (Nobel for Chemistry 1995 together with M. Molina and F.S. Rowland); however, special circumstances are required for this reaction to arise (3).

2.0 DEPOSIT, MINERALOGY, AND CHEMICAL PROCESSES

2.1 Deposit

The primary sedimentary deposit of kaolin sand of Hirschau- Schnaittenbach was formed about 220 million years ago, during the Low Triassic period. From the Eastern and Southern Bavarian mountains, the great rivers carried gneiss and granite gravel down to the great Hirschau-schnaittenbach basin, gradually filling it up. The broken-up rock, swept along by the rivers, already partly prepared mechanically, underwent further attrition as a result of the acid phreatic waters. In this process, the sodium feldspars became almost wholly kaolinized, while the sodium feldspars were only partially kaolinized. Thus, in this case, one can also speak of quartz or arcose feldspar sands. Kaolinization was only partial, so that besides small quantities of light-coloured mica, potassium feldspar in particular withstood the transformation, which was one of the reasons that has allowed AKW-Kick GmbH to become the largest producer of potassium feldspar in Europe. The deposit has an extension of 6 km, from Hirschau in the west to Schnaittenbach in the east, and exhibits a clear stratification as a result of the various particle sizes and mineralogical compositions. This layer of kaolinized quartz feldspar is 30-40 metres thick, and has an 8-10 deg. south-north slope.

2.2 Mineralogy

The larger grains are mostly quartz; feldspars are less often encountered. Kaolin prevails in the clay fraction, besides muscovite and illite, with a particle size of 0.001 mm to 0.06 mm, and a major fraction of 6 to 20 microns. The feldspar is basically made up of orthoclase. Its particle-size distribution exhibits a bell-shaped curve, with a maximum width of 0.1-0.4 mm and limits between 0.002 mm and 2 mm. The raw earth that is taken from the mine contains 6-12% feldspar, 10-14% kaolin, 70-80% quartz, 1-2% mica, and less than 1% accompanying minerals. The most important accompanying minerals are: anatase, biotite, goethite, hematite, ilmenite, monazite, rutile, tourmaline, xenotime and zirconium.

3.0 PREPARATION

The mineral mix is subjected to a settling process, to separate out the larger quartz sand fractions. Using multiple separating steps, each mineral is enriched in a sophisticated hydrocyclone facility and separated into different product flows. In one of the last preparation steps, the quartz and kaolin feldspar concentrates are freed of heavy metals and oxide impurities, and separated into kaolin, feldspar and quartz sand. The feldspar and quartz exhibit a negative zeta potential across almost the whole pH range (4). However, the accompanying minerals that contain iron and titanium exhibit a positive surface charge to acid pH (5); thus, by floatation and the addition of anion-active collectors for a pH<3, the minerals are separated, which during firing might give rise to undesired colouring. Thanks to this procedure, impurities are removed from the system, which contain iron, such as hematite and goethite, and TiO_2 carriers such as anatase, leucoxene and ilmenite. The selective separation of feldspar and quartz is performed by activating the former with fluoride ions to acid pH, with subsequent cation flotation (6 and 7). This is a direct flotation. We have called this product FS 900 S. By means of an oxide flotation to acid pH followed by a feldspar flotation, in two steps, with subsequent cleaning, a feldspar product can be extracted with a total feldspar content of over 93%.

Another high-quality feldspar product is obtained by indirect flotation, which we shall call «FS 900 FS» hereinafter. This feldspar is characterized above all by its fine grain structure and even lower Fe_2O_3 and TiO_2 contents. This lower content is obtained by an anionic flotation variant. Suitably selecting anion-active detergents, besides decreasing the heavy metal content, allows depleting the quartz and kaolin accompanying minerals, which represent the most important elements of the flotation charge. The following table shows the two-step flotation development for the feldspar designated FS 900 SF hereinafter.

Chemical analysis	1st flotation step	2nd flotation step	FS 900 SF feldspar
	%	%	%
SiO_2	67,7	69,1	66,9
Al_2O_3	17,5	16,2	17,3
Fe_2O_3	0,16	0,037	0,03
TiO_2	0,60	0,03	0,02
CaO	0,02	0,03	0,03
MgO	0,04	0,01	0,01
N_2O	0,53	0,65	0,79
K_2O	11.30	13.17	14.29
P_2O_5	0,08	0,08	0,08
BaO	0,25	0,28	0,31
L.O.I.	1.65	0.36	0.18

For the user, the different ways of preparing FS 900 S and FS 900 SF entail different product characteristics. At first sight, highly enriched feldspars are involved, with a high alkali content. The potassium feldspar/sodium feldspar ratio is about 13:1. A basic difference between FS 900 S and FS 900 SF is due to the totally different flotation methods involved. In the case of FS 900 SF, detergent adsorption can only be conducted electrostatically in positive adsorption areas of the mineral, whereas in the case of feldspar FS 900 S, a bond is involved, which is formed by chemical adsorption of the cationic detergents to activated surface areas. This is also shown in the value of COD: While in the FS 900 S, values are found between 0.10-0.12% for O_2, in the case of FS 900 SF they are only 0.02-0.05% for O_2. The new type FS 900 SF, extracted by anionic flotation and virtually free from harmful substances, completes the supply chain for the frit and glaze producing industry, which uses potassium feldspars with low sodium, iron and heavy metal contents. Continuous quality control, including in production process management, ensures constant product quality.

4.0 PHYSICAL CHARACTERISTICS AND ADVANTAGES OF POTASSIUM FELDSPARS FROM HIRSCHAU.

The most significant features of these feldspars may be generally summed up as follows:

- High Al_2O_3 content - High K_2O content - Low Na_2O content - Very low Fe_2O_3 and TiO_2 contents - Constant chemical composition - Good particle distribution - Uniform white crystalline colour on firing- Wide melting interval - Virtually negligible pollution levels.

The flotation processes used for obtaining potassium feldspars 900 S and 900 SF yield excellent starting particle sizes for the ceramic applications indicated above. Particle-size distribution ranges from 150-20 microns (recognized today as being the most suitable size for frit fusion)(8).

RESULTS AND CONCLUSIONS:

- Potassium feldspars produced at HIRSCHAU exhibit high potassium and aluminium contents, low sodium contents and only traces of iron and titanium.

- Owing to the sophisticated hydrocyclone process, and advanced flotation techniques, a highly appropriate particle-size distribution is obtained for frit and glaze fusion.

- The high K_2O content allows the eutectic with sodium feldspar to be easily formulated (ratio 1:2), which sinters at 1075°C (very useful for porcelain tile bodies)(9 and 10).

- The balanced chemical composition and K_2O/Al_2O_3 ratio allows formulating special crystalline glaze compositions for fast single firing, with clear savings in calcined alumina and potassium carbonate and nitrate.

- From an ecological point of view, it has been shown that potassium feldspar 900 SF is the least pollutant product in firing processes.

- Product quality is backed by the Company Registry Certificate awarded in accordance with International Standard ISO 9001 (EN 29001).

- Surface tension of glazes with K_2O is around 15 times less than that of glazes prepared with Na_2O. This quality, together with high viscosity in the melt, allows obtaining smooth surfaces without the small depressions that impair gloss (11).

References

(1) SINGER F., SINGER S.S. - Cerámica Industrial, I, pp. 124 (1971)
(2) RIESENFELD E. - Tratado de Química Inorgánica, p. 468 (1948)
(3) ABC CULTURAL no. 206, p.53 (995)
(4) JAKOBS U. - Doctoral dissertation, University of Regensburg (1993)
(5) NEY P. - Zetapotentiale u. Flotierbarkeit von Mineralien, Springer Verlag, Vienna, New York
(6) SCHUBERT U., ABIDO A.M. - Bergakademie, 19 (10)(1967), p.601
(7) SMITH R.W. - Soc. Ming. Eng., AIME 232, p.160 (1965)
(8) FERRER R.F. «ESMALTES CERAMICOS PARA MONOCOCCION», p. 7 (1988)
(9) TABLAS CERAMICAS - I.Q.T. TECNOLOGIA CERAMICA, p.4.19 (1984)
(10) JOUENNE C.A. - Traité de Céramique et Materiaux Mineraux p. 94 (1979)
(11) TABLAS CERAMICAS - I.Q.T. TECHNOLOGIA CERAMICA, p. 7.3 (1984)