



	<b>Experiment title:</b> Identification and kinetics of formation of non-metal impurity species in molten cryolite electrolyte - case of sulfur, silicon and phosphorus compounds	<b>Experiment number:</b> CH-3745
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: April 15 to: April 19, 2013	<b>Date of report:</b> Feb 28, 2014
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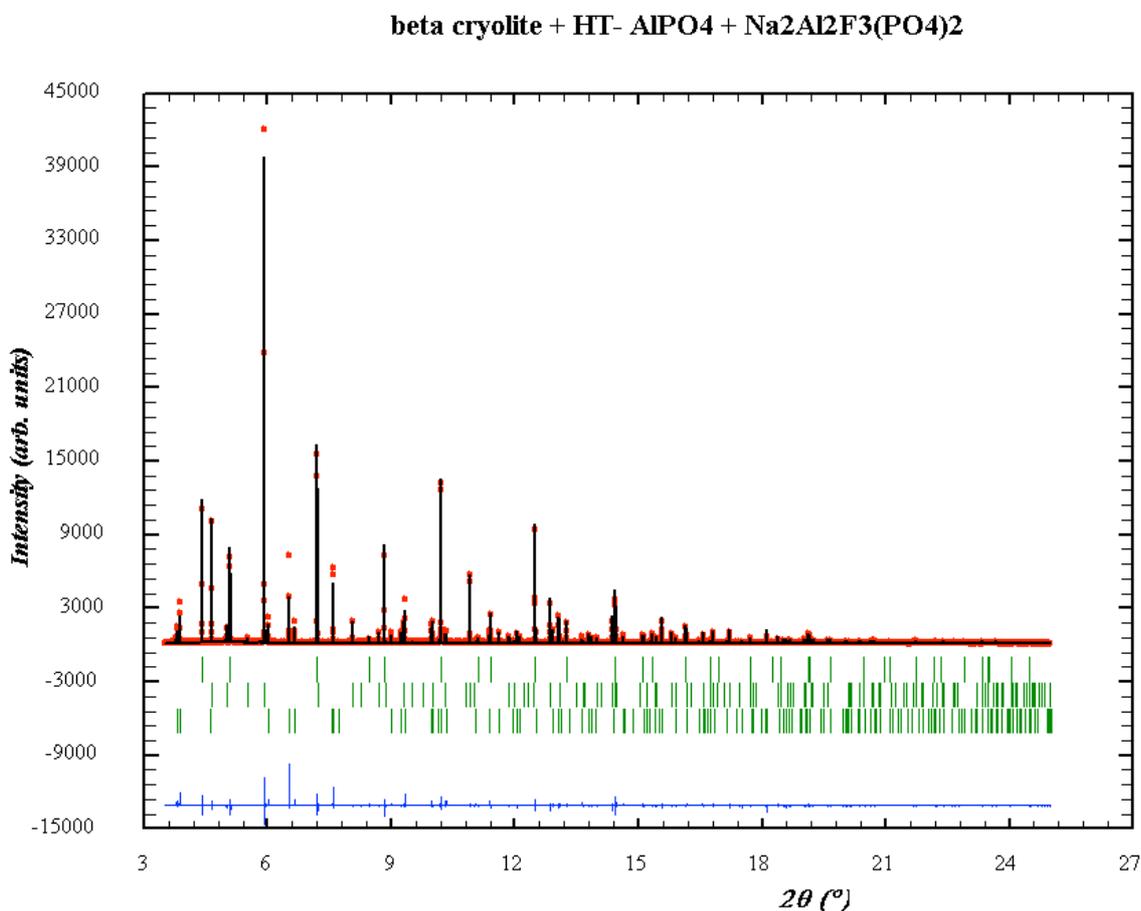
**Report:**

Electrolytes in commercial cells for production of aluminium always contain impurities based on phosphorous, silicon, sulphur, iron, vanadium, titanium, chromium, nickel, copper, cadmium, gallium, etc., which are introduced through alumina feeding, carbon anode consumption, use of tools. The constitution of these compounds-impurities dissolved in cryolite-based melts is essentially unknown, despite they have considerable influence on many technological and environmental aspects of the process (contamination of primary aluminium, pollution of greenhouse gases like SO<sub>2</sub>, COS, CS<sub>2</sub> and H<sub>2</sub>S), current and energy efficiency. Impurity species in the electrolyte may participate in various types of reactions, especially of redox kind. Although it is assumed that some particles containing impurities are volatile or entrained in the gas stream without reacting with the electrolyte, it is also expected that their major part reacts with the electrolyte and dissolves in it. In the past years, physico-chemical (density, viscosity, surface tension, electrical conductivity) and thermodynamic (phase diagrams) studies oriented to phosphorus and silicon impurities dissolved in cryolite have been completed in our Laboratory . The main problem of all these analyses however is that although they provide useful physicochemical data, the information on phase composition derived from them is only indirect and in many cases just approximate.

Analyzed samples were divided into two groups. The first contained the samples heated above the melting point of cryolite prior to arrival to ESRF. The second group contains just the mixtures of raw materials (NaF, AlF<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, AlPO<sub>4</sub> and amorphous SiO<sub>2</sub>). While the first group was meant just for phase analysis, the

second was used for collecting of data on reaction mechanism. Because analysis of the first group required just 600°C to transform monoclinic alpha- to beta-cryolite (monoclinic to pseudocubic to unmask other phases in the patterns), the samples were filled in quartz capillaries and heated by hot air blower. The second group required temperatures above 1000°C to complete synthesis, so that the samples were mounted in sapphire capillaries and heated by halogen lamps. The halogen lamp furnace was prior to heating the samples calibrated by measuring the lattice parameter of platinum. This calibration showed remarkable discrepancy between the temperature set on the controls and real values. Those differences were attributed to ageing of halogen lamps.

Preliminary results have showed that phase analysis of the sample with SiO<sub>2</sub> do not reveal any recrystallization of silicon oxide, which could hence be present either in unreacted state or in an amorphous compound. Melting cryolite with AlPO<sub>4</sub> resulted in a multiphase system containing beta-cryolite, traces of NaF, unreacted AlPO<sub>4</sub> and, quite surprisingly, newly created Na<sub>3</sub>Al<sub>2</sub>F<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> phase.



Analysis of the mixtures with Na<sub>2</sub>SO<sub>4</sub> reveal its transformation and formation of new crystalline phases. Examination of the data taken from the samples heated with halogen lamps is due to its complexity still in progress.