Assessment of the Thermodynamic Stability of Thermal Insulating Materials in Aluminium Electrolysis Cells

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Abstract

The cathode bottom lining in aluminium electrolysis cells serves as a thermal insulating barrier and is important for the overall thermal and dimensional stability of the cell. The thermal insulation layer is protected against chemical degradation by a refractory layer, but due to recent technological developments and new cell designs, the stability of insulating materials is expected to become an important matter of concern in the years to come. The thermodynamic stability of thermal insulating materials in chemical environment corresponding to the one below the carbon cathode has been assessed. Thermodynamic evaluation was used to predict possible chemical reactions caused by sodium vapour, which possibly can penetrate through the refractory barrier and react with the insulation material. The most likely chemical reactions with the insulation materials were identified by minimization of Gibbs energy of the system. Changes in the mineralogical composition of the insulation materials were predicted based on the thermodynamic calculations. The structural integrity of the thermal insulation materials is discussed in relation to the mineralogical changes predicted based on the thermodynamic assessment.

Keywords: Thermal insulating materials; aluminium electrolysis cell; thermodynamic stability; degradation.

1. Introduction

The process of producing aluminium by molten salt electrolysis is energy demanding, and a considerable amount of the energy input is lost in the form of heat release to the surroundings [1]. The electrolysis cells are designed with sidewalls of materials having high thermal conductivity in order to form a frozen layer of bath, the sideledge, which will protect the sidelining and potshell from the corrosive nature of the bath. The bottom of the cell is designed in such a way to minimize energy loss by using a layer of materials with low thermal conductivity in the bottom lining, below the refractory layer [2]. The thermal insulation layer will also reduce possible solidification of the bath towards the cathode [1]. The most typical thermal insulating materials used in this layer are moler (diatomite), calcium silicate, or vermiculite based materials [2]. The thermal insulating layer is critical for the overall thermal and dimensional stability of the cell [1, 2]. A layer of refractory materials is placed above the insulating layer in order to protect it from bath components or volatile species that may penetrate through the carbon cathode blocks [2].

At present, the cell lifetime is in most cases limited by the carbon cathode wear [3]. The cathode wear and reduced lifetime of the cells have become a major challenge as the industry have progressed towards high amperage cells [3, 4]. Increased lifetime of the cells can be achieved by increasing the carbon cathode thickness on the expense of the refractory layer. This will put higher demand on the thermal insulating layer, and may increase the exposure to gas species such as Na and $NaAlF_4$, which can react with the highly porous insulation material with dramatic changes in the thermal conductivity and the thermal profile of the cell and, consequently, the energy loss. The stability of the thermal insulation materials have not received much attention in the literature [5, 6], but the forecast to reduce the thickness of the refractory layer actuates the understanding of the chemical and thermal stability. In addition, the shift towards lean cells (low energy cells) will require better insulated cells, as less heat is generated to maintain operational temperature. Evidently, in this case, the heat gradient will increase towards the insulation.

Sodium vapour is most likely [7, 8] the first chemical species diffusing through the refractory layer. Mineralogical changes in the materials due to reaction with sodium are investigated by computational thermodynamics for diatomite, calcium silicate and vermiculite based materials. The findings are discussed with respect to the chemical stability and structural integrity of the thermal insulation layer in the electrolysis cells.

2. Method

The thermodynamic assessment of the different insulation materials was carried out by use of equilibrium calculations, through minimization of Gibb's energy, in the thermochemical software FactSage^{TM} (version 7.0). This software contains various modules and databases and allows the user to do various equilibrium calculations [9]. In this work, the *Equilibrium* module has been used in combination with the *FactPS* database to analyse the phase composition of the insulation materials during increasing amounts of sodium vapour. The weight percent chemical composition of calcium silicate, vermiculite, and moler materials investigated are presented in Table 1. A simplified composition of each material, where any oxide below 4 wt% has been disregarded, has also been analysed and is listed with a superscript "a" in the same table. Including the loss on ignition (LOI), the mass sums up to approximately 100 wt% for the full composition of all three materials, and a little less for the simplified compositions. This was used as input in the software, i.e. the simplified compositions have slightly less starting mass than the full compositions. The calculations were performed at a temperature of 970 °C, which is higher than the more common 850 °C isotherm in today's operating cells. However, with decreasing thickness of the refractory layer the insulation layer isotherm is bound to increase. Additionally, all main phases were the same at 850 °C. Solid phases with amount less than 1 wt% are not shown in the figures.

Table 1. Chemical composition of the different insulation materials investigated.

Product	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	SO_3	LOI*
Calcium silicate	47	0.3	0.3	0.6	45	0.1	0.1	N/A	6
Calcium silicate^a	47	0	0	0	45	0	0	N/A	N/A
Vermiculite	47	7	4	21	2	0.5	11	N/A	7
Vermiculite^a	47	7	0	21	0	0	11	N/A	N/A
Moler	77	9	7	1.3	0.8	0.6	1.5	1.2	1.5
Moler^a	77	9	7	0	0	0	0	0	N/A

LOI*: Loss on ignition given at 1025 °C.

^{a}: Simplified composition, i.e. any oxide below 4 wt% is disregarded in the calculation.

3. Results

3.1. Calcium silicate materials

Calcium silicate is mainly silica and lime, with only small fractions of other oxide impurities. The content of other phases in calcium silicate is therefore minor and does not influence

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7. References

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