

KINETICS OF SPODUMENE RECRYSTALLISATION

Bogdan Z. Dlugogorski, ^bArif A. Abdullah, ^cHans Oskierski, and ^dGamini Senanayake

Energy and Resources Institute, Charles Darwin University, Casuarina Campu, Australia

^bDepartment of Chemical Engineering, Oil Projects Company (SCOP), Ministry of Oil, Iraq

^oSustainable Geochemistry and Mineral Science, Harry Butler Institute, Murdoch University, Australia

^dCollege of Science, Technology, Engineering and Mathematics (STEM), Murdoch University, Australia

Presenter and Corresponding Author

Bogdan Dlugogorski

ABSTRACT

In this presentation, we will review the kinetic models that cast the decrepitation of α -spodumene to β spodumene [1-4] in terms of simple, and easy to apply, mathematical equations. We will also provide the predictions from the models, as shown in Fig. 1, for typical operating conditions of the kilns in lithium refineries. Such predictions could serve to optimise the kilns, and therefore to assist in the decarbonisation of spodumene processing. Two of the models [2,3] derive from the X-ray diffraction (XRD) measurements, allowing predictions of the formation of both γ - and β -spodumene from two tandem reactions:

$$\alpha$$
-spod $\rightarrow \varphi \beta$ -spod + $(1 - \varphi) \gamma$ -spod $(k_1), \gamma$ -spod $\rightarrow \beta$ -spod (k_2) (1)

where, φ is the selectivity parameter that typically falls between 0.3 and 0.5. The kinetic rates (k_1 and k_2) correspond to the products of the Arrhenius formula and the first order reaction model:

$$k_1 = A_1 \exp(-E_1/(R T))C_{\alpha}$$
 and $k_2 = A_2 \exp(-E_2/(R T))C_{\gamma}$ (2)

where, E and A have their traditional meaning of the activation energy and the frequency factor, respectively, and C_{α} , C_{γ} and R reflect the mass fraction of α -spodumene and γ -spodumene and the ideal gas constant, in that order. Typical values of the Arrhenius constants are 780 kJ mol⁻¹ and 75 for $E_{1,2}$ and $\ln(A_{1,2}/\min^{-1})$, respectively [2]. The more recent work of Fosu et al. quotes E_1 and E_2 as 655 kJ mol⁻¹ and 730 kJ mol⁻¹, correspondingly, as well as $\ln(A_1/\min^{-1}) = 59.3$ and $\ln(A_2/\min^{-1}) = 63.7$. In contrast, the models based on the heat measurements in the DTA (differential thermal analyser) [1] and DSC (differential scanning calorimeter) [4] consider the spodumene recrystallisation process to proceed in an idealised one-step unimolecular reaction, which, for the model of Botto et al. [1], comprises $E = 275 \text{ kJ mol}^{-1}$ and $\ln(A/\min^{-1}) = 25.3$:

> α -spod $\rightarrow \beta$ -spod, with the *k* = Aexp(-*E*/(*R T*))*C*_{α} (3)

> > As evident in Fig. 1, the models of Fosu et al. [3] and

Abdullah et al. [4] yield pragmatic predictions of the

decrepitation time required for the complete

recrystallisation of α -spodumene to β -spodumene.

They also comprise physically meaningful values of

the rate parameters. Evidently, it takes substantially

longer to convert v- to β -spodumene than just to

convert α -spodumene to its products [2,3]. The

industrially-relevant

The model of Abdullah et al. makes fA and E to be functions of conversion, where f is the reaction model [4].



model of Moore et al. [2], developed for particle sizes of around 5 µm, leads to predictions of unrealistically 100.0000 short heating time for spodumene particles.

Keywords: Lithium refining; Reconstructive transformation; Phase change; Lithium chemicals

- [1] I. Botto, S. Cohen Arazi, T.G. Krenkel, Bol. Soc. Esp. Cerám. Vidr. 14 (1975) 433-40 (in Spanish).
- [2] R.L. Moore, J.P. Mann, A. Montoya, B.S. Haynes, Phys. Chem. Chem. Phys. 20 (2018) 10753-10761.
- [3] A.Y. Fosu, N. Kanari, D. Bartier, H. Hodge, J. Vaughan, A. Chagnes, Materials 14 (2021) 7423.
- [4] A.A. Abdullah, B. Z Dlugogorski, H.C. Oskierski, G. Senanayake, In preparation