

Alumina microstructure and its properties as an adsorbate: an example of research at the Light Metals Research Centre

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Introduction

Aluminium is ubiquitous in our modern world, with its global importance and utility reflected in the 50 metric megatonnes of primary metal produced worldwide during 2013,¹ and at least that quantity again produced through recycling. Primary metal is produced exclusively by the Hall-Héroult process in which alumina (Al_2O_3) is electrolytically reduced after dissolution in molten cryolite (Na_3AlF_6). To feed this demand, approximately 107 metric megatonnes of alumina were produced² worldwide during 2013 with the vast majority (~94 %) used in primary metal production.

Al_2O_3 plays an interesting dual role in the Hall-Héroult process; it is used not only as the feedstock, but as an adsorbate in dry-scrubbing systems for the capture of volatile fluorides, including the extremely toxic compound HF which is generated during electrolysis. This reacted alumina is ultimately fed into the electrolysis cells, providing an effective means of recycling fluoride, thereby dramatically reducing one of the industry's major feedstocks. However, with rising pressures on the industry, particularly concerning energy consumption (more than 2 % of the world's electric power is consumed by the Hall-Héroult process), increasing metal production by way of higher amperages has led to challenges in maintaining the fluoride balance in some smelters. With excess fluoride (concentrations of AlF_3 in excess of that expected in strictly stoichiometric cryolite) being intimately related to, and indeed used specifically to control, cell temperatures and ultimately process efficiency, and with problems associated with maintaining fluoride emissions below government mandated thresholds, the adsorption properties of alumina are becoming increasingly important to the industry as a whole. Understanding the mechanism of HF adsorption and subsequent reaction on the alumina has therefore been of considerable interest.

Complicating matters for studies relevant to the aluminium industry, smelter grade aluminas (SGAs) span a wide range of particle morphologies and crystallographic phases, which influence (amongst other properties), the pore characteristics of the final material.

The Light Metals Research Centre (LMRC) at the University of Auckland has long had an interest in this area. In this paper we discuss two examples of recent research we have undertaken regarding the impacts of alumina properties, particularly regarding its role as an adsorbent, on significant problems in the aluminium industry. These examples are the application of laboratory-based approaches to explore the fundamentals of the fluoride adsorption capacity of alumina, and working with indus-

trial partners to understand the impacts of these phenomena on the smelter fluoride cycle, a large scale real-world problem.

Light Metals Research Centre (LMRC)

Founded in 2002 based on the research histories of Professors Barry Welch, John Chen, Margaret Hyland and Jim Metson, and Academic Director Mark Taylor, the LMRC at the University of Auckland has established an international reputation for world-leading expertise in the alumina refining and primary aluminium smelting industries. LMRC focusses on providing independent research and development capabilities, consulting services as well as industry-relevant training programmes such as the successful Postgraduate Certificate in Light Metals Reduction Technology from the University of Auckland. Since its inception, LMRC has seen the founding academic staff more involved in leading and guiding research more fundamental in nature, while still maintaining strong ties to the other centre activities. Indeed, LMRC has co-hosted a number of postgraduate students in areas of fundamental research such as alumina properties, gas adsorption and electrolyte chemistry, supervised within the Departments of Chemical and Materials Engineering and the School of Chemical Sciences. The centre is currently overseen by its Director, Mark Dorreen, with managers Pre-tesh Patel looking after all projects in Europe and the Gulf regions, Yashuang Gao responsible for those in China, and Ron Etzion for modelling and fundamental research.

LMRC is also involved in the development and commercialisation of technologies within the centre and with partner companies. One example is Shell Heat Exchanger (SHE) technology, currently undergoing extended performance trials on a group of pots in an operating smelter in Germany. Originally designed for efficient air-driven cooling of the reduction cell sidewall, essential for operation at increased amperage and metal production, it is now also being trialled for heat retention during periods of decreased amperage to allow stable operation while accommodating deep power modulation. Similarly, we are currently commercializing a comprehensive smelter operation, control and management supervisory software package, Gen3. This suite is designed to address a wide range of smelter management issues, provide early detection of abnormalities, improved smelter efficiency, reduction of emissions, increase pot lifetimes, and optimise staff performance and utilisation. In performance trials Gen3 has brought improvements of +1% current efficiency and -100kWhr/kg Al.

October of 2014 saw LMRC relocate its facilities from the city campus to the University's newly-opened Newmar-

ket campus. Located at the former site of Lion Breweries, the new campus accommodates staff and research students spanning a range of engineering and science disciplines, with LMRC amongst the first groups to relocate. This has provided LMRC with generous new laboratory space including a general wet chemistry laboratory, a dedicated HF laboratory for testing the kinetics and capacity of the adsorption of HF by alumina (Fig. 1), a designated area for a suite of furnaces and high temperature research equipment such as a full sized sidewall rig for SHE testing, an analytical laboratory including XRD, LECO oxygen analyser, FT-IR, and N₂ physisorption capabilities, and a dedicated workshop.



Fig. 1. The new HF adsorption facility

Smelter grade aluminas (SGA): materials properties and pore structure

The properties of the SGAs trace from those of the aluminium hydroxide from which they are derived. The hydroxide, gibbsite, is produced by the Bayer process in which bauxite is dissolved in heated NaOH solution, with Al(OH)₃ subsequently crystallised from a purified sodium aluminate solution. SGA growth is dominated by particle aggregation (being considerably faster than direct crystal growth), with strategies concerning the crystal seeding and control of the precipitation conditions dictating, amongst other properties, particle size. This ultimately impacts the phase composition of the final material following calcination. Alumina during the middle stages of calcination can span a wide range of largely defect spinel structures, collectively termed the transition aluminas, with γ -, γ' -, δ -, and θ -Al₂O₃ structures particularly common in the SGAs. The fully calcined hexagonal α -phase (corundum) typically constitutes only a few percent of the final product. The phases listed are in order of decreasing residual hydroxide content, with the phase distribution dictated by calcination conditions, primarily temperature and time. Extremes of phases are associated with negative impacts on the smelting process: the relatively under-calcined γ -Al₂O₃ has been associated with increased HF generation;^{3,4} on the other hand, the over-calcined α -Al₂O₃ is the least soluble polymorph leading to undissolved alumina settling out onto the cathode of the reduction cell, with the ultimate consequence being significant energy losses due to increased electrical resistance.

Industrial stationary calciners, the biggest of which range in capacity from 3 to 4,000 T/day, strive for high throughput and low energy consumption, which has the potential for under- or over-calcination of the gibbsite (particularly the fine material). However, heat transfer into the cores of the finer particles is obviously much more rapid than in larger grains, and these materials can therefore be converted almost entirely to α -Al₂O₃. Environmental scanning electron microscopy (ESEM) is a powerful tool for visualising the relationship between phase and particle size. Using charge contrast techniques,^{5,6} for example, readily charging α -Al₂O₃ can be easily identified as bright white particles providing immediate visual evidence that, indeed, it is typically only the smallest particles (<50 μ m in diameter) that tend to be dominated by this phase (Fig. 2). As a consequence of the range of particle sizes, and hence phases, that may be adopted, SGAs are often very complex, multifaceted materials.

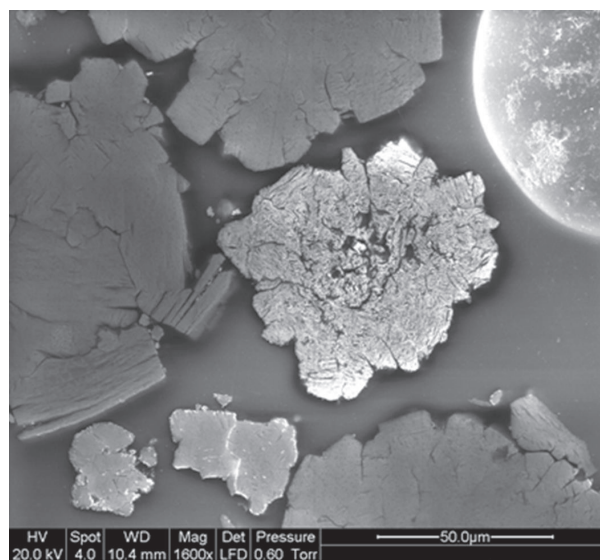


Fig. 2. ESEM image of α -Al₂O₃ grain (white)

The phase distribution has far-reaching impacts on other particle properties, as each phase has associated with it unique average pore size and surface area characteristics. From under- to over-calcined alumina, specific surface areas (SSAs) drop whilst average pore diameter increases.⁴ In terms of an adsorbent/dry scrubbing agent, a shift toward under-calcined materials such as γ -Al₂O₃, with a BET (Brunauer-Emmett-Teller) SSA of ~ 300 m² g⁻¹, should ostensibly be favoured (industrial SGAs typically possess SSAs of 70-80 m² g⁻¹). Indeed, high BET surface area for increased adsorbate capture is a desired quality for general adsorbents. However, in the particular case of alumina, the residual hydroxide makes these phases a potent source of HF^{3,4}. It might be thought that the increase in HF generated may be off-set by the increased SSA/scrubbing capacity. However, there has been growing evidence that the smallest pores may be inaccessible in industrial scrubbers due to kinetic limitations.^{7,8} Where the balance lies, given the role of alumina both in generating and recycling fluorides, is therefore an important question to the industry.

HF adsorption

Some insight into the role of kinetically restricted access to the pores should be obtained by consideration of the mechanism of the HF-surface interaction; these insights might also be expected to be of wider relevance to general adsorbate-adsorbent systems. Such systems are generally assumed to interact by the formation of adsorbent mono- and multilayer(s) and the Al_2O_3 -HF system is no exception.⁹⁻¹¹ Indeed, the initial adsorption interaction is followed rapidly by an annealing reaction, irreversibly capturing the HF on the alumina surface. This should therefore be observed in a characteristic perturbation to the pore structure of scrubbed aluminas. Pore size distributions (PSDs) have been obtained by application of the Barrett-Joyner-Halenda (BJH) method¹² during N_2 physisorption measurements on unreacted (primary) SGAs, or prim- Al_2O_3 . This approach starts by measuring the liquid volumes lost from an N_2 -saturated adsorbent at a given pressure, which is being incrementally reduced, with large pores losing their N_2 adsorbate at higher pressures than smaller ones. Assuming pores are cylindrical, the pore diameter of the smallest empty pore is obtained solely from the current pressure (by way of the modified Rayleigh equation). Then, with the adsorbate volume lost in a given pressure decrement equated with the volume of the emptied pore, it is trivial to deduce an effective length.¹³ Consequently, one can extract the complete geometries of a discrete set of representative cylindrical pores.

Owing to an irreversible reaction with HF,¹⁴ these measurements may also be performed on the scrubbed (secondary) aluminas, sec- Al_2O_3 . This allows adsorption models to be directly tested; a fortuitous circumstance as a general adsorbate-adsorbent system may not survive the sample pretreatment conditions needed prior to measurement. For example, consider monolayer formation (Fig. 3a). A pore of diameter D in prim- Al_2O_3 shrinks by twice the monolayer thickness, $2t_m$, after scrubbing; this has an easily reconstructable effect on pore geometry. Applying these perturbations to the pores of pre-dosed materials, we can derive the PSD expected for materials following treatment with HF, and compare these directly to measurement.

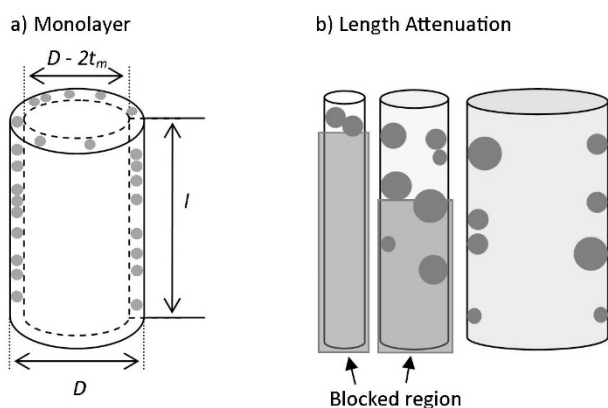


Fig. 3. Models of HF adsorption on alumina.

To test this, we first require a dosed sec- Al_2O_3 . These are readily synthesized in the HF dosing rig pictured in

Fig. 1. Briefly, several grams of alumina are placed in a heated reaction vessel (inside the oven, in the fume-hood), and anhydrous HF passed through the chamber. A Boreal laser detection system measures HF in the flue gas; experiments are said to have reached break-through when non-zero HF concentrations are detected, and saturation when concentrations reach that of the inlet gas, i.e. no appreciable scrubbing is occurring. A great deal regarding kinetics and scrubbing capacity can be learnt from experiments where aluminas are exposed to varying quantities of HF (particularly as a function of time); it should be noted that the PSDs shown in this article apply to materials treated to saturation loadings of HF.

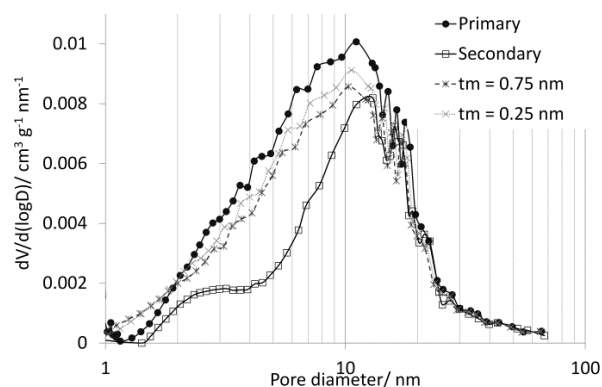


Fig. 4. Monolayer model results for HF adsorption impacts on pore size distributions.

The PSDs of typical SGAs, and the results of several monolayer models (with various estimates of t_m) are presented in Fig. 4. It is clear that monolayer models are inadequate to describe adsorption. In particular, increasing monolayer thickness cannot explain the emergence of a knee observed in the secondary material around 3-4 nm. This indicates that scrubbing slows, and therefore the PSD changes little from the original, in pores of this approximate size, and provides the first direct evidence of kinetically inaccessible pores.^{15,16} Extending models to include kinetically restricted access to the pores, one can create two subsets of pore lengths, $L_p(D)$, for accessed and restricted pores (larger or smaller than some threshold pore diameter, D_{thresh}), respectively. We chose the following model for this partitioning:

$$L_p(D \geq D_{thresh}) = \frac{L_p(D)}{2} \left[1 + \operatorname{erf} \left(\frac{D - D_{thresh}}{\sqrt{2}\sigma} \right) \right] \quad 1$$

$$L_p(D \leq D_{thresh}) = L_p(D) - L_p(D \geq D_{thresh}) \quad 2$$

Pores larger than D_{thresh} (eqn (1)) have the monolayer model applied, the remainder left unmodified; following which the modified pores are then rebinned into a single distribution – see Fig. 5 for a schematic description of this partitioning process. The term D_{thresh} is a fitted term, expected to be ~ 3 nm – the position of the knee in Fig. 4; however, even with this rather contrived device, it was still found that the PSDs of secondary aluminas could not be adequately modelled.¹⁵

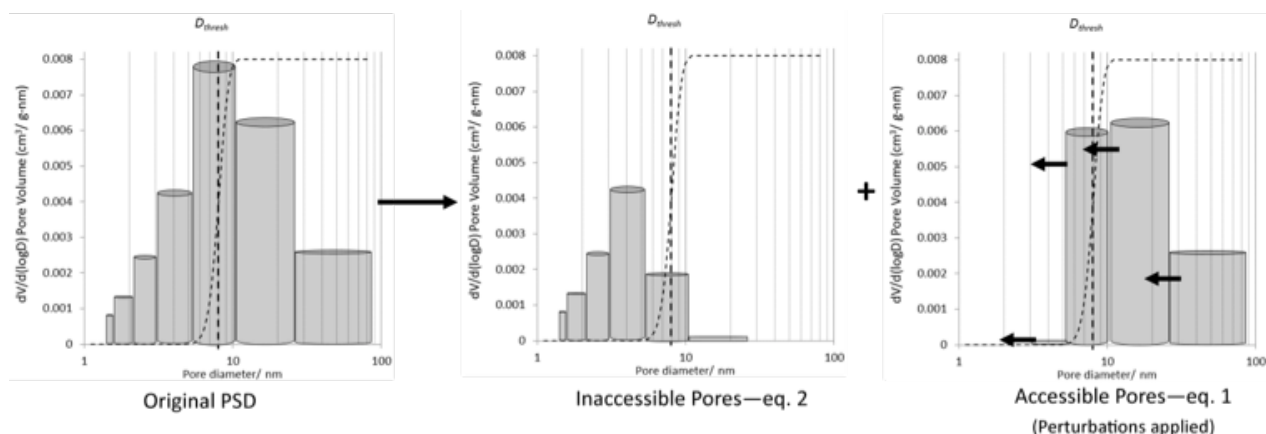


Fig. 5. Schematic representation of pore partitioning - see equations 1 and 2.

A more sophisticated model was subsequently developed considering instead pore blocking and length attenuation as the primary loss of pore volume/surface area (Fig. 3b). Assuming some normally-distributed variability in adsorbate thickness (t_m), which may include variability in pore diameter itself, a more rigorous probabilistic model was constructed¹⁵ based on the random doping of surface sites. When two sites on opposing sides of a pore wall were within $2t_m$ apart, the pore is potentially blocked and, assuming closed pores, any pore length below the blocking point was lost. For example, it was possible to show that pore lengths in a kinetically accessible region were attenuated as:¹⁵

$$L_{\text{sec}}(D) = A([\text{HF}])L_{\text{prim}}(D) \left[1 + \text{erf} \left(\frac{2t_m - D}{\sqrt{2}\sigma} \right) \right] \quad 3$$

$A([\text{HF}])$ is an as-yet unspecified function of HF concentration whose value increases with either concentration or exposure time (i.e. pore lengths shorten more with increased HF exposure), and σ is the standard deviation in adsorbate thickness. The functions for dividing pores into accessible and inaccessible regions, eqtns (1) and (2), were used again, but within this model their mathematical forms could be rigorously justified.¹⁵ As can be seen in Fig. 6 this model very faithfully reproduces the PSDs, indicating pore attenuation and not monolayer formation limits the scrubbing capacity of aluminas. Further, adsorbate thickness could be extracted after fitting the model form to the experimental data; modelling several aluminas (including industrial materials) a layer thickness estimate of (0.69 ± 0.24) nm was obtained, in excellent agreement with previous estimates obtained by very different procedures at $(0.65 - 0.83)$ nm.¹⁰ The position of the knee, where the transition from accessible to inaccessible pores occurs, is found to be $2.7 - 2.8$ nm based on model fitting results.¹⁵ As the models make no assumptions specific to the HF- Al_2O_3 system, these are very likely general phenomenon in adsorbate-adsorbent systems.

Fluoride recycling

The HF- Al_2O_3 system also provides a powerful example of how the mechanism of interaction in adsorbate-adsorbent systems can have important consequences on application; namely through the recycling of fluoride in

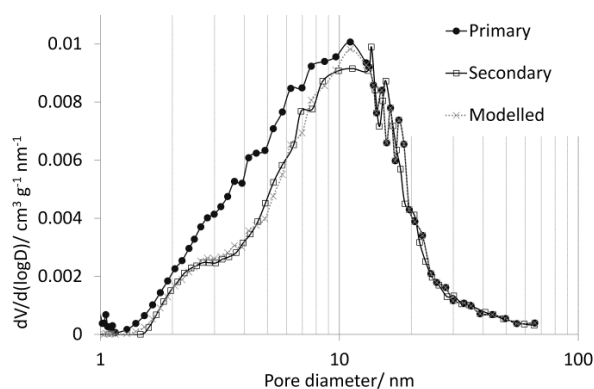


Fig. 6. Attenuation model results for HF adsorption impacts on pore size distributions.

the aluminium smelter, which plays a crucial role in energy consumption and materials feeds. As noted earlier, aluminium reduction is undertaken in a Na_3AlF_6 electrolyte; however, feeds of AlF_3 are commonly added to depress the liquidus temperature (freezing point) of the electrolyte and limit aluminium solubility. This allows a cell to be run at lower temperatures, and given the energy consumption intrinsic to the process, such savings are vital. However, a change in the fluoride concentration has a number of important negative impacts on the cell. A decrease in AlF_3 content increases the liquidus, which ultimately increases the cell operating temperature; this in turn makes the metal produced (which separates from the electrolyte when formed) more soluble in the electrolyte and susceptible to re-oxidation. On the other hand, too great an AlF_3 content reduces the solubility of Al_2O_3 , which can settle on the cathode and (being an insulator) increases the cell resistance (and temperature) and therefore energy consumption. The balance is clearly very important, but is becoming extremely difficult to maintain, given the current drive to run higher amperages to produce more metal. Cell temperatures and dissolved AlF_3 concentration are intimately balanced; the cell walls have adhered a ledge of frozen (almost pure) cryolite, with liquidus and temperature changes leading to ledge freezing/melting, and therefore AlF_3 concentration/dilution. Clearly, the loss of volatile fluorides in the flue gases will therefore have a significant impact on AlF_3 content, and its incomplete return by way of adsorbate on the alumina makes maintaining the important fluoride balance extremely challenging.

To better understand these properties, given the number of interacting parameters involved, lab-based studies clearly have limitations. An extensive sampling campaign was therefore undertaken in Germany with the support of industrial partners Trimet Aluminium SE and Outotec GmbH. A range of aluminas (produced by differing calciner technologies and therefore possessing unique phase/pore size distributions) were sampled and a large number of smelter-recorded parameters (cell temperatures, alumina/ AlF_3 feed quantities, applied voltages, metrics of cell stability, concentrations of HF in the flue gases) were collected. Integrating these parameters over 60 cells each, and over 24 hour periods over approximately 20 months, plant data were obtained which could be correlated against various alumina properties as determined by XRD and N_2 physisorption measurements, for example. In particular, several measures of SSA were examined to best assess the adsorption characteristics of alumina.

Extracting the influence of alumina properties on key performance measures has required multiple regression analyses. Several regression models of bath acidity (the concentration of excess AlF_3 in the electrolyte) were constructed,¹⁷ ultimately employing all cell parameters listed, the concentration of $\alpha\text{-Al}_2\text{O}_3$, and an SSA parameter as independent variables. The significance of each variable was assessed by its P -value, computed during the regression analysis; any variable with $P > 0.05$ (i.e. adopting a 95 % confidence level) was deemed insignificant, and therefore removed. This process of modelling followed by variable removal was iterated until all remaining variables were deemed significant.

Particularly interesting for the adsorbate-adsorbent interaction is the role of surface area metrics in these models. The BET method¹⁸ is arguably the most widely employed model for determining surface areas of powdered materials. This model is an extension of the Langmuir approach to accommodate multilayer formation, in which the number of physisorbed probe molecules required to cover the surface, and the cross-sectional area of each probe, allows the total adsorbent surface area to be deduced.¹³ The BET method does not allow one to distinguish the contributions of pores of different sizes, with any pore large enough to accommodate the probe molecule measured. However, the BJH method also allows for the determination of surface areas; with the diameters and lengths of the pores known, the surface area of each pore is easily derived, with total surface area obtained by summing over the pores. Careful choice of this summation range therefore allows the role of fine pores to be investigated.

To investigate the importance of the adsorbate-adsorbent interaction, models inclusive of all cell parameters, but focusing on surface area as the sole alumina property, were constructed. BET surface areas were used, as were various BJH estimates where the lower-bound of the summed pore size (x – see Fig. 7) was allowed to vary from the 1.7 nm typically employed. That is, $\text{BJH}(x - 300)$ represents the total BJH surface area of pores between x and 300 nm in diameter. In particular, we allowed x to increase, to explore removing the contribution of the

smallest pores, suggested to be kinetically prohibited from reacting by PSD modelling results, from the surface area estimates. The P -value for each predictor, modelled in turn, is plotted as a function of x (the smallest pore diameter included in the surface area estimate) in Fig. 7.

Clearly, the BET areas are statistically insignificant, i.e. there is no correlation between BET surface area and the concentration of AlF_3 in the electrolyte. However, BJH-based surface areas all demonstrate statistical significance as these measurements explicitly remove the contribution of fine pores which, as we demonstrated in the preceding section, should be inaccessible to the adsorbate. Further, a lower bound on the pore size giving the most significant predictor lies between 3 – 3.5 nm, corresponding almost exactly with the knee in the sec- Al_2O_3 PSD of Fig. 6 (representing the boundary between the accessible and kinetically inaccessible porosity) and in very good agreement with our model results. This strongly indicates that including porosity below this limit simply constitutes noise in the model, obscuring the importance of the alumina in carrying fluoride back to the reduction cell. This is demonstrated by the BET-based models, where differences in surface area/adsorbate carrying capacity of different aluminas is found to have no significant influence on the AlF_3 concentration in the electrolyte as these surface area estimates are heavily dominated by the contribution of fine (micro)pores. More generally, this provides independent verification for the role of transport kinetics and pore blocking (rather than simple availability of adsorption sites) in the activity of adsorbents, and the significant impacts this can have on real world processes.

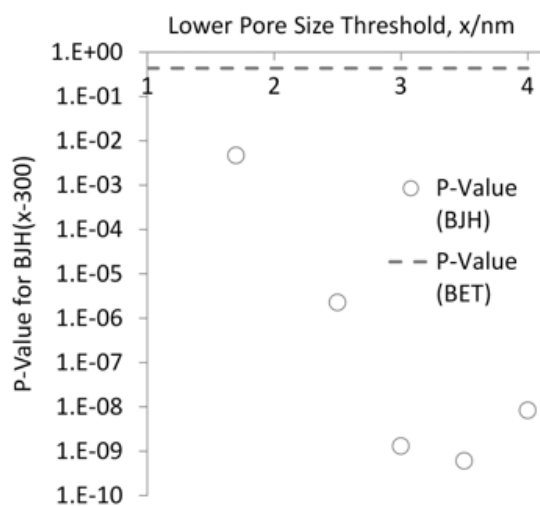


Fig. 7. P -value of SSA predictors in AlF_3 regression models.

Conclusions

In addition to its role as a feedstock in the aluminium industry, alumina plays a crucial role as an adsorbent in dryscrubbing cell gases. This system, while of considerable practical importance to the smelter, also provides a useful test bed to examine important features of adsorbate-adsorbent systems. A fundamental laboratory-based approach has shown that a simple monolayer-based model of capture on adsorbate surfaces is not always the most realistic approach; issues of surface accessibility, either

by kinetic restrictions or pore blocking, can also manifest in specific effects, and these are observed in the HF-Al₂O₃ system.

The return of fluorides to the electrolysis cell by the alumina adsorbate is found to have a clear relationship with surface area measurements that specifically remove pores shown in the lab-based studies to be inaccessible on kinetic grounds. This ultimately has significant impacts on the smelting process in terms of the consumption of materials and energy, which imposes significant monetary costs. This provides an example of the impacts of subtle fundamental processes at the molecular level on chemistry performed in industry on extremely large scales.

Acknowledgements

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