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EFFECTS OF COMPOSITION AND GRANULOMETRY ON THERMAL CONDUCTIVITY OF ANODE COVER MATERIALS

Hasini Wijayaratne[1], Margaret Hyland[1], Mark Taylor[1], Andreea Grama[2], Tania Groutso[1]
[1]Light Metals Research Centre, The University of Auckland, Private Bag 92019, New Zealand
[2]Department of Chemical & Materials Engineering, The University of Auckland, Private Bag 92019, New Zealand

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Abstract

Thermal conductivity of anode cover material is critical in determining cell top heat loss. It has been observed that thermal conductivity of cover material is strongly dependent on packing and particle size distribution. Granular material that is densely packed (lower voidage) has higher thermal conductivity. When two sizes of spherical particles are mixed at various size ratios, the theoretical voidage can be reduced from 0.4 to 0.2-0.3. This can be applied to a particle system of crushed bath and alumina that constitute cover material. Currently, many smelters produce cover material that is too fine with high voidages. This has the effect of lowering the thermal conductivity which can cause unnecessary operational problems within the cell. Additionally, the effect of cover composition on thermal conductivity is not obvious. This paper describes studies conducted in the laboratory to understand the effects of composition and voidage on thermal conductivity of cover material.

Introduction

Anode cover is a crucial part of an aluminium reduction cell because of its important role in maintaining overall heat balance, protecting the carbon anode from air burn, and controlling fluoride loss. Control of anode cover material properties such as composition, depth and granulometry provide means of optimising the top heat losses in the cell. Due to the increase in line current over the years in the reduction cell technology, heat generation inside the cells has increased. This has led to higher service temperatures of both the anode assembly and anode cover material which needs to be controlled through optimising anode cover [1].

The effective thermal conductivity of cover material determines its capacity to dissipate heat through the top of the cell. It is an important property that is useful in modeling the heat flows through the top of the cell, predicting the thermal and structural stability of the cover material. For example, highly insulating anode cover material with low thermal conductivity will over heat the cover, leading to partial melting and subsequent collapsing due to chiolite phase melting inside the cover. In contrast, extremely conductive material will dissipate increased amounts of heat from the top of the cell leading to operational problems such as low bath temperature, low alumina dissolution, increased side ledge thickness leading to overall heat imbalance in the cell. Anode cover in an aluminium reduction cell consists of two distinct layers; a top layer of granular anode cover material and a bottom layer consisting of a consolidated crust formed due to exposure to heat and fluoride fumes over time.

Previous studies have focused on properties of mainly alumina based anode cover materials and in particular alumina based consolidated crusts. Hatem et al. measured thermal conductivity of various alumina based crusts and alumina powders and observed that there is a relationship between crust density and thermal conductivity [2]. Dependence of thermal conductivity on the bulk density of consolidated anode cover crusts was also suggested by Richards [3]. A correlation between bulk density of anode cover crust and alumina content was observed by Liu et al. indicating that density and proportion of alumina are determining factors of thermal conductivity [4]. However, relatively limited studies have been conducted on crushed bath based granular cover and consolidated anode cover crust materials [1, 5].

Apelt [6] and Shen [7] obtained thermal conductivity values for crushed bath based granular cover and alumina, which were an order of magnitude lower than those measured for crust materials by Hatem et al [2, 6, 7]. Thus, it is understood that the granular cover layer is the controlling factor which determines the top heat losses of the cell.

Figure 1 illustrates the different factors that affect thermal conductivity of cover material. Granulometry, or more precisely, voidage, is a major factor, as demonstrated by Shen [7]. For example, for fine crushed bath with a voidage of 45%, thermal conductivity was measured to be 0.5W/m°C while for coarse crushed bath with a voidage of 35%, thermal conductivity was measured to be 0.7W/m°C [7]. However, the effect of voidage on thermal conductivity is not simple and is affected by other factors such as particle size that contributes to the voidage. Literature related to heat transfer in packed beds, suggest that relatively large particles at high temperatures can give rise to radiation effects [8]. Specifically, Schotte [9] observed radiation effects, for 1mm particles above 400°C and for 100μm particles above 1500°C. This supports studies of Yagi and Kunii, where the radiation contribution to thermal conductivity was found to be as high as 80% for large particles measured at 840°C (which was the highest temperature measurement) [9, 10]. These imply the complexity of heat transfer through powder systems of varying particle sizes and indicate the interrelated nature of particle size, voidage and packing density as well as temperature, all of which contribute to thermal conductivity.

This demonstrates the importance for modern smelters for achieving the right granulometry to avoid operational problems such as crust melting from beneath due to over insulating nature of poor cover material. An example of this is shown in Figure 2. However, many smelters are equipped with autogenous mills for bath processing and these are known to produce excessively fine bath material. This has led to smelters facing challenges in obtaining the correct granulometry necessary for optimum anode cover material.

This paper aims to discuss the findings of a rigorous study conducted in the laboratory to understand the effects of granulometry and composition, (which are the two main control parameters used in anode cover design) on thermal conductivity of granular anode cover materials. This paper also aims to discuss practical implications of the findings for smelters in obtaining the ideal anode cover material and provides a basis for further studies.

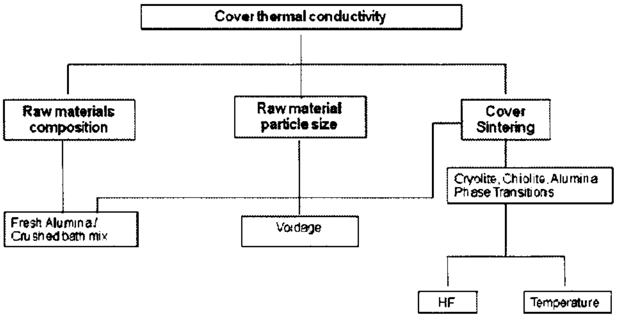

Figure 1: Factors affecting cover material thermal conductivity.

Figure 2: Crust collapsed from beneath due to over insulating nature of fine cover [1].

Experimental

Materials

Industrial granular anode cover material and processed crushed bath from two different smelters, referred to as Smelter 1 and Smelter 2 respectively were used for experiments during this study.

Methods

Both anode cover and processed crushed bath bulk samples as received from the respective smelters were size fractionated into 'coarse', 'intermediate' and 'fine' size fractions. The size fractions were defined as coarse being above 4mm, intermediate being between 1-4mm and fine being below 150µm. The Smelter 1 bulk sample was more homogenously mixed with fine material whereas Smelter 2 crushed bath bulk sample was predominantly coarse material. The fraction between 150µm and 1mm is recognized to be part of the intermediate size fraction, however has not been used in this particular set of experiments. This is because the objective of this study was to establish distinct size fractions, which would give distinctly different thermal conductivity values.

The voidage of each sample was calculated using equation (1) with measured values of 'as poured' bulk density (ρ_b) and true density (ρ_t).

$$Voidage = \frac{\rho_t - \rho_b}{\rho_t} \times 100 \qquad (1)$$

Semi-quantitative phase composition of cover and crushed bath samples were determined by X-ray Power Diffraction.

Thermal conductivity measurements of each material were obtained using an apparatus developed by Shen based on the Fourier's law of heat conduction [7]. According to Fourier's law, this method relies on establishing a temperature gradient across the sample of interest and measuring the heat flux required to maintain that gradient at steady state. As long as uni-dimensional heat transfer is ensured, this enables the calculation of thermal conductivity of the sample. For a system where one dimensional heat transfer occurs in the radial direction, heat transfer can be described as shown in equation (2):

$$q_r = -\lambda \frac{dT}{dr} \qquad (2)$$

Where;
q_r is the heat flux at steady state, λ is thermal conductivity of material and dT/dr is the temperature gradient across a known radial thickness of the sample.
Figure 3 shows a schematic of the apparatus which is of a concentric cylindrical setup. It consists of an inner heating core with a smaller diameter (d) and an outer cylindrical heating shell of larger diameter (D). A radial temperature gradient of approximately 60°C was set up between the inner heating element (T_H) and the outer heating element (T_L) during experimental runs. The granular material to be measured was packed inside the cylindrical cavity between the two heating surfaces as shown in Figure 3. At steady state, measurements were recorded and results obtained were used in calculating the thermal conductivity of the material (λ) according to equation (3) which is the integrated form of the heat transfer equation indicated by equation (2).

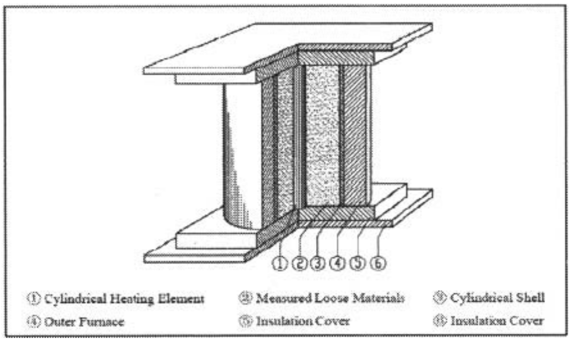

Figure 3: Schematic diagram showing the cross section of the cylindrical thermal conductivity apparatus.

$$\lambda = \frac{Q}{2\pi L(T_H - T_L)} \ln\left(\frac{D}{d}\right) \qquad (3)$$

It is to be noted that, all thermal conductivity data presented in this paper are plotted as relative (normalized to coarse crushed bath) and not as absolute data.

Results and Discussion

The purpose of this study was to determine the effects of particle size distribution, voidage and composition on thermal conductivity of granular material. Figure 4 shows the semi-quantitative phase composition results obtained for both bulk and size fractionated samples from each smelter. Alumina composition is also indicated as a comparison for the fine materials. Samples labeled as 'cover material' was received already blended with alumina, whereas samples labeled 'crushed bath' was received unblended with alumina. All samples shown in Figure 4 were used 'as received', apart from size fractionating and no further blending of alumina was performed in the laboratory.

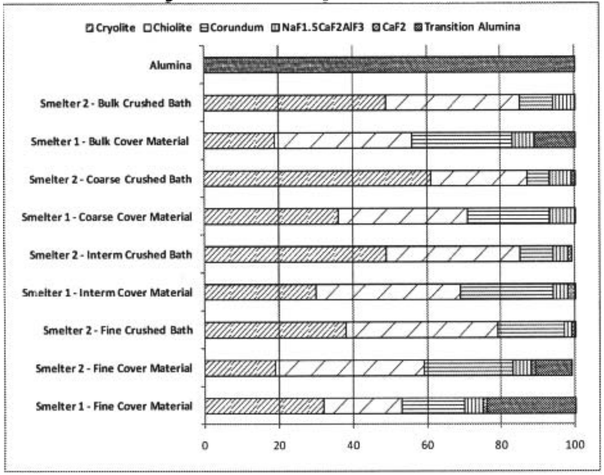

Figure 4: Semi-quantitative X-ray phase composition data of crushed bath and cover materials as a function of size fraction.

In general, composition of crushed bath and anode cover varies with size fraction. For example, alumina is concentrated in the fine fraction in the cover material, which is to be expected. In contrast, coarse materials tend to have larger quantities of cryolite and chiolite phases and only trace levels of transition alumina (which were not quantifiable by X-ray diffraction).

<u>Fine Material (Below 150µm)</u>

Phase composition data plotted in Figure 4 indicates that the four fine materials have quite different compositions. Smelter 1 fine cover material has higher quantities of cryolite and transition alumina compared to Smelter 2 fine cover material. Smelter 2 fine crushed bath and fine cover material have similar quantities of chiolite, however varying amounts of corundum and other bath phases.

Figure 5 shows the thermal conductivity data plotted for the four fine samples including multiple data points for alumina showing the reproducibility of multiple measurements. Reproducibility of thermal conductivity is reasonable and the variation between measurements is in the range of 0.1% to 2.0%.

It is clear from this plot that all samples have very similar thermal conductivity, despite the differences in composition of these materials. Table I shows that the density and voidage values of the fine materials from both smelters lie in the range of 59 to 62% with alumina voidage being slightly higher. Since, all four samples have particle sizes below 150microns, radiation effects cannot be expected at the measurement temperature range, as suggested by Schotte [9]. Therefore, the corresponding voidages can be expected to be insulating. This corresponds well with the thermal conductivity data for these materials which fall almost on the same line in Figure 5.

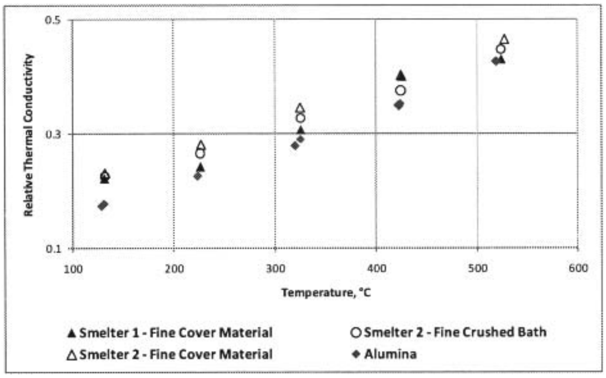

Figure 5: Relative thermal conductivity data obtained for Smelter 1 and 2 fine materials and for alumina.

Table I: Density and voidage measurements obtained for all bulk and size fractionated samples.

Sample	Bulk Density (g/cm³)	True Density (g/cm³)	Voidage (%)
Smelter 1 - Fine Cover Material	1.14	2.84	60
Smelter 2 - Fine Cover Material	0.98	2.56	62
Smelter 2 - Fine Crushed Bath	1.18	2.90	59
Alumina	0.98	2.67	63
Smelter 1 - Interm Cover Material	1.51	2.88	48
Smelter 2 - Interm Crushed Bath	1.34	2.88	53
Smelter 1 - Coarse Cover Material	1.40	3.06	54
Smelter 2 - Coarse Crushed Bath	1.29	3.06	58
Smelter 1 - Bulk Cover Material	1.75	3.07	43
Smelter 2 - Bulk Crushed Bath	1.43	2.97	52

<u>Intermediate Material (Between 1- 4mm)</u>

The cover and crushed bath intermediate fractions differ in both composition and voidage. In particular, amounts of cryolite and corundum are significantly different when comparing the two samples. In addition, Smelter 1 sample has a lower voidage due to its relatively high packing density.

Figure 6 shows the thermal conductivities of both intermediate size samples, with data for Smelter 2 fine crushed bath also plotted for comparison. The thermal conductivities of the intermediate materials are notably higher than the fine materials, as might be expected on the basis of lower voidage of the intermediate materials. In addition, it is probable that radiation effects begin to make contributions to the thermal conductivity at higher temperatures at this intermediate particle size [9], as can be seen by the higher slopes of the thermal conductivity lines, compared to the fine material. The two intermediate samples have similar thermal conductivities; however, Smelter 1 cover material has a slightly higher thermal conductivity than Smelter 2 crushed bath sample. This can be expected because of the relatively lower voidage and higher bulk density of Smelter 1 sample.

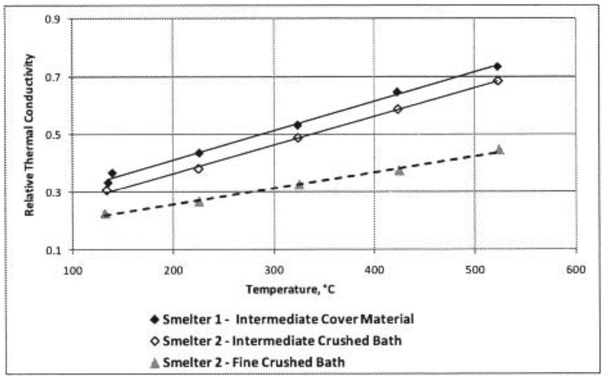

Figure 6: Relative thermal conductivity data obtained for Smelter 1 and 2 intermediate materials as well as Smelter 2 fine crushed bath plotted for comparison.

Coarse Material (Above 4mm)

The coarse fraction of both smelter samples have notable differences in phase composition as can be seen from Figure 4. Smelter 2 coarse crushed bath sample has a larger sum of bath phases and less corundum compared to Smelter 1 coarse sample. According to Table I, bulk density and voidage values for the two samples are also different as the calculated uncertainty based on instrumental uncertainty for each voidage value is ±0.5%. However, it is interesting to note that the thermal conductivity values plotted in Figure 7 for these samples are nearly identical as can be seen by the overlapping data points. Again, the coarse materials have higher thermal conductivities compared to both intermediate and fine materials (plotted with dashed lines for comparison). Similarly, the rate of increase of thermal conductivity of the coarse materials with temperature is also higher than both intermediate and fine materials. This phenomenon observed even with relatively high voidages (refer coarse material voidages in Table I) suggest radiation effects contributing to thermal conductivity as demonstrated by previous workers studying heat transfer through packed beds of large particles [8-10].

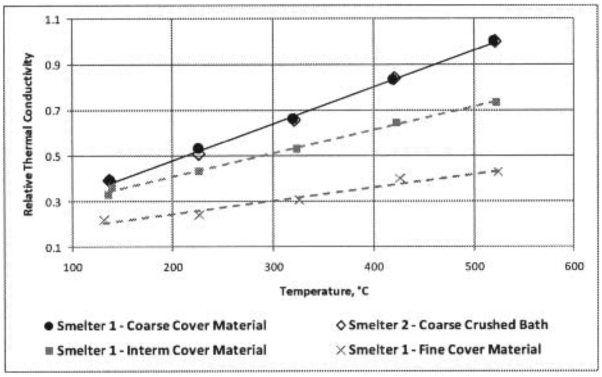

Figure 7: Relative thermal conductivity data obtained for Smelter 1 and 2 coarse materials together with Smelter 1 intermediated and fine cover data plotted for comparison.

Bulk Material

Initial phase compositional analysis performed on bulk materials before size fractionating also show differences in phase composition. This is to be expected as Smelter 1 bulk sample is a cover material which includes blended smelter grade alumina while Smelter 2 bulk sample consists of pure crushed bath with only trace levels of transition alumina. Bulk density and voidage values listed in Table I also indicate clear differences between the samples, with Smelter 1 sample having a lower voidage. This is to be expected as Smelter 1 sample included noticeably more fine material homogenously mixed with coarse material which contributes to the higher packing density. This relates to the two particle packing theory which indicates how voidage can be significantly reduced by mixing two particles of different sizes in specific size ratios as shown by Figure 8 [5, 11].

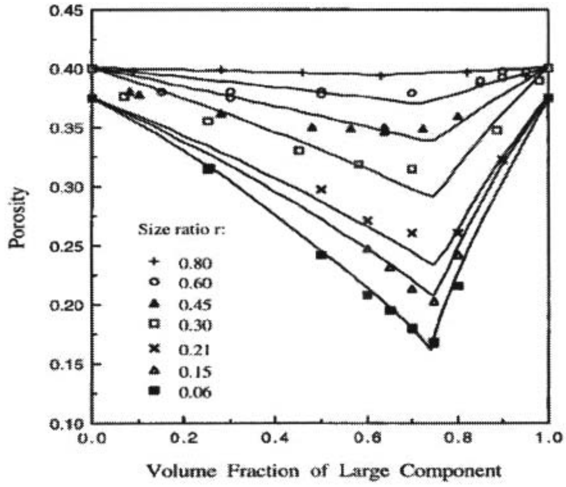

Figure 8:Porosity against volume fraction of large component, showing the effect of reduction in voidage due to mixing two particles at specific size ratios [11].

Thermal conductivity data obtained for the bulk samples are plotted in Figure 9.

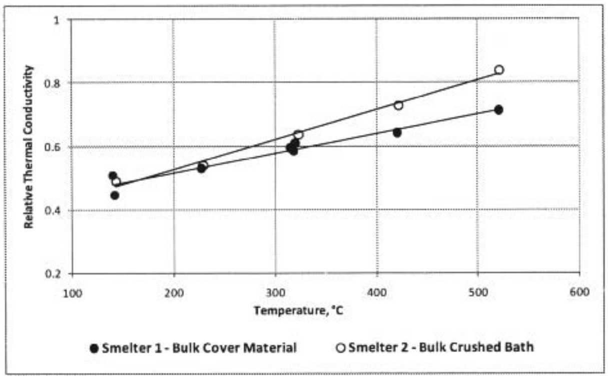

Figure 9: Relative thermal conductivity data obtained for Smelter 1 and 2 bulk materials.

Although each bulk sample has a different composition and granulometry, it is interesting to note that both samples have very similar thermal conductivities up to approximately 320°C. Above this temperature, Smelter 2 sample thermal conductivity begins to increase with respect to Smelter 1 sample. This behavior of Smelter 2 sample is very interesting as having a higher voidage compared to Smelter 1 sample; it is expected to be lower in conductivity. However, as can be seen from Figure 8, higher voidages can be expected even when the coarse particles are in high proportions (above 0.9 volume fraction) and this effect was also observed with the coarse samples. Kunii and Smith suggest that radiation effects can become significant in packed beds of relatively large particles above 900°F (approx 482°C) [8]. Shen observed the same affect (above 400°C) in particular with samples having voidages greater than 40% [7]. Therefore, it is possible that heat transfer within the thermal conductivity measuring apparatus (which is essentially a packed bed of granular particles) is affected by radiation at higher temperatures when particles are relatively large which contributes to high voidage (as in the case with Smelter 2 bulk sample which consists largely of coarse material) resulting in a corresponding increased thermal conductivity.

Mixed Samples using Smelter 2 Crushed bath and Alumina

In order to understand the effect of cover blend composition on thermal conductivity, coarse crushed bath from Smelter 2 was blended with comparable proportions of alumina and fine crushed bath material from the same smelter. The blend compositions and corresponding density and voidage data are listed in Table II. The corresponding thermal conductivity data for these samples are plotted in Figure 10.

It is to be noted that the sample labelled with adjacent notation (<200micron) is a sample that contain large quantities of fine material (in particular -45microns particles) in the fine portion. In order to see the effect of removing this ultrafine portion from the fines, the same composition blend was prepared by removing the -45micron fraction. This is distinguished by the label (45-150micron) adjacent to the sample name (See Table II and Figure 10).

Table II: Density and voidage measurements obtained for mixed samples.

Sample	Bulk Density (g/cm³)	True Density (g/cm³)	Voidage (%)
60% Coarse Crushed Bath + 40% Alumina (45-150micron)	1.63	2.83	42
40% Coarse Crushed Bath + 60% Alumina (45-150micron)	1.54	2.67	42
40% Coarse Crushed Bath +60% Fine Crushed Bath (45-150 micron)	1.38	2.38	42
40% Coarse Crushed Bath +60% Fine Crushed Bath (<200micron)	1.53	2.96	48

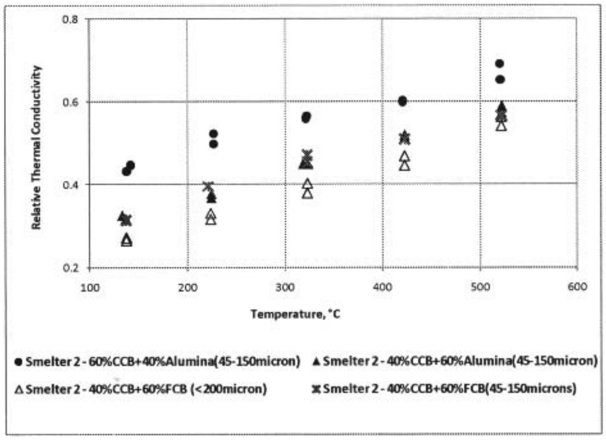

Figure 10: Relative thermal conductivity data for the mixed crushed bath samples.

Data plotted in Figure 10 show interesting features. When a mixed sample has coarse bath in a proportion of 60% blended with 40% alumina, the thermal conductivity of the sample is higher than for a sample blend of 40% coarse crushed bath and 60%alumina. This can be expected due to the relatively higher packing density of the 60%coarse bath and 40%alumina sample, although both samples have the same voidage. This suggests that voidage alone does not determine thermal conductivity when the cover blend contains coarse material in the higher proportion as other factors such as radiation can contribute to thermal conductivity.

In addition, it is clear from Figure 10 that the thermal conductivity of 40%coarse bath and 60%fine bath (45-150microns) is nearly identical to that of the 40%coarse bath and 60% alumina blend. However, thermal conductivity of the sample with ultrafine bath (<200micron sample) is comparatively slightly lower, as can be expected from its corresponding higher voidage. This suggests that when cover blends contain fine material in the larger proportion, voidage can predominantly determine thermal conductivity as other factors such as radiation are not as important.

These results clearly illustrate that in a sample consisting of a blend of coarse and fine particles, thermal conductivity is determined by granulometry rather than by composition. This means that in a blend of cover material, coarse crushed bath can be blended with either alumina or fine bath as long as each of these fine material have the same particle size distribution. In either case, thermal properties will be very similar. However, the relative proportions of coarse to fine material blended in the cover will determine to what extent, the corresponding voidages created within the material will aid heat transfer.

This suggests that particle size has a more pronounced effect on thermal conductivity than composition of granular anode cover materials. However, as the granular cover sinters due to exposure to heat and fumes within the cell over time, phase transformations occur dynamically changing the structure of the consolidating crust. In addition, when temperatures exceed 600°C, cover components such as chiolite phase may melt and as a result properties of the material would radically change.

Implications for Smelters

The trends observed with the laboratory studies conducted, have relevant implications for smelters.

More thermally conductive cover material can be prepared using coarse bath in a higher proportion in the cover mixture, with a lower proportion of fine material to give higher packing density and reduced voidage. This supports a theoretically based conclusion reached by the authors earlier [5]. In this case the fine fraction can be made up of either alumina or fine bath. Increasing the proportion of fine material in the blend will contribute to lowering the thermal conductivity and ultrafine fine bath material aids further deterioration of thermal conductivity.

These findings are significant for smelters as this indicates the importance of controlling granulometry of cover material and in particular the generation of fines. Uncontrolled fine fraction in cover material will have the effect of decreasing thermal conductivity, especially when more fine material is added in the form of alumina without consideration of how much fines is already present in the base material.

However, there is likely to be a 'critical' proportion of smelter grade alumina that is necessary in cover material, in order to ensure sufficient structural strength in the resulting consolidated crust. Determining the ideal proportion of alumina to be blended with cover was outside the scope of the current study since this requires study of the higher temperature behavior of the crust material over time. Separate studies are needed for understanding this issue and the findings of this paper will be a firm basis for further studies in this regard.

Although the loose cover material layer is the controlling factor that determines immediate heat losses from the cell, it is also important to understand the thermal properties of consolidated crusts over a longer period of time; in particular modern day crushed bath based crusts which have not been widely studied. The key to understanding the thermal conductivity of consolidated crusts lies in understanding the evolution of voidage and phase transformations during the consolidation process, which need to be further investigated.

These will contribute to the ongoing development of the understanding necessary for anode cover material design for modern smelters.

Conclusions

Laboratory studies have been conducted in order to understand the effects of granulometry and composition on thermal conductivity of granular cover materials. It is clear that, granulometry or particle size distribution has a more significant effect on the effective thermal conductivity of cover mixtures than composition.

In general, higher proportions of coarse bath in a cover mixture increase the effective thermal conductivity whereas a higher proportion of fine material (either alumina or bath fines) lowers the effective thermal conductivity.

Controlling the granulometry of cover material, in particular the fines generated is found to be critical as it contributes to lowering the overall thermal conductivity of the cover. This has very important implications for smelters in that the amount of alumina blended with cover material needs to be controlled (as it contributes to the proportion of fine material), especially in the case of crushed bath from autogenous mills which produce excessive fines.

These findings provide a firm basis for further studies such as, determining the critical amount of alumina required for structural strength in cover and evolution of thermal properties of consolidated crushed bath based crusts over time.

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