RECENT DEVELOPMENTS IN STANDARD PROCEDURES FOR THE ANALYSIS AND TESTING OF SMELTER GRADE ALUMINA

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ABSTRACT

Standards Australia committee MN/9 - (Alumina and Materials Used in the Production of Aluminium) was formed in 1983 in response to requests from the alumina and aluminium industries in Australia for standardised analytical procedures and test methods for measurement of physical and chemical properties of alumina. From 1983 to 1995 the committee has published seven alumina standard methods covering the topics of loss of mass on ignition, percent minus 20 micron content, alpha alumina content, specific surface area, angle of flow, particle size distribution by electroformed sieves and trace elements by x-ray fluorescence. This paper reviews some of the principles involved in the development of these analytical procedures and test methods. The current work program is also discussed. These methods and the ongoing development and review program provided by MN/9 are meeting the industries' need for up-to-date, relevant standard methods.

KEY WORDS:
Alumina Methods Standards Australia

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1.0 INTRODUCTION

The need to develop a comprehensive set of up-to-date, high quality standard methods for the analysis of Smelting Grade Alumina was identified as a priority by representatives of the Australian Alumina and Aluminium industries in the early 1980s. Standards Australia and representatives of these industries formed a committee under the auspices of Standards Australia to meet this need. The committee is comprised of leading technical experts in alumina analysis from all of the smelting grade alumina producers and users in Australia, with organisational support provided by Standards Australia. The early activities of the committee, "MN/9 - Alumina and Materials Used in the Production of Aluminium ", has been described previously (1st International Alumina Quality Workshop, 1988).

The standard methods developed are subjected to rigorous technical evaluation and inter-laboratory testing before publication. All of the published methods include comprehensive details of the technical basis of the method, the equipment required, the procedures to be followed, and a statistical evaluation of the results expressed in terms of the intra-laboratory repeatability (r) and the inter-laboratory reproducibilty (R). Additional information is also given as required to assist the analyst. Since precision is generally a function of the absolute value of the quantity determined. Therefore a table of values for the precision of the parameter being determined. Precisions as determined by the inter-laboratory tests are normally quoted for several aluminas which are selected to provide a range for the parameter of interest.

The methods published by this committee are the seven parts of the Standards Australia standard - AS2879.

Part 1 Determination of loss of mass at 300° C and 1000° C
Part 2 Determination of particles passing a 20 micron sieve
Part 3 Determination of alpha alumina content by X-ray diffraction
Part 4 Determination of specific surface area by nitrogen adsorption
Part 5 Determination of angle of flow
Part 6 Determination of the mass distribution of particles sizes using electroformed sieves.
Part 7 Determination of trace elements - wavelength dispersive x-ray fluorescence spectrometric method (DRAFT FORMAT)

Of the methods published the two which the committee consider worthy of special mention are the particle size method and the soon to be published method for trace elements in alumina by XRF.

Since size distribution and chemical composition are the two major issues in any specification for an alumina. These methods provide the data that is fundamental to the certification of alumina quality. These standards break new ground technically in being first principle methods that do not rely on the existe nce of accurately determined standard samples for calibration.

2.0 REVIEW OF METHODS AND PROCEDURES PUBLISHED SINCE 1988

2.1 AS2879 Part 2 Determination of particles passing a 20 micron sieve

This method was published after a detailed review of methods used by participants as well as an ISO draft procedure. In this method two test portions are weighed out into platinum crucibles. One portion is set aside into a desiccator while the other is used in the sieving process. The sieving process involves washing the sample with acetone across a certified electroformed 20 um sieve. During the washing process the sample is also carefully brushed across the screen with a fine soft brush. The material that is retained on the sieve is quantitatively transferred back to it's platinum crucible. The acetone is carefully evaporated and then both portions of the test sample (sieved and non sieved) are ignited at 300° C. The test portions are then cooled in a desiccator and the mass of particles passing 20 microns is calculated.

The method differs from other methods in that the test portions are ignited to 300° C. The errors introduced by not doing this were considered to be significant.

Table 1
Precision Data For -20 Micron Determination

Mean -20 micron content %m/m	Repeatability r	Reproducibility R
1.4	0.22	0.56
.4.4	0.17	1.05
5.7	0.52	1.17
6.1	0.29	1.16

2.2 AS2879 Part 3 Determination of Alpha Alumina content by X-ray diffraction

The method involves ratioing the integrated peak area of the (012) lattice plane reflection for the test portion to a 100% alpha alumina standard. Through a number of test programs the committee examined different methods of sample preparation, diffraction peaks used and methods for the calculation of results.

The method recommends against purchasing an external 100% alpha alumina standard for use, as they were found to be of variable quality. Rather, a method for producing a 100% alpha standard in-house was specified. After testing several procedures the starting material for this is a sample of material similar to that which is to be tested.

By following this procedure, the subsequent determination by XRD yields excellent accuracy and precision, as shown below.

Table 2
Precision Data For Alpha Alumina Determination

Mean alpha alumina content %	Repeatability r	Reproducibility R
4	0.5	0.6
5	0.5	0.6
7	0.3	0.7
15	0.6	1.1
17	1.3	1.5
27	1.6	2.4
42	2.9	3.5

Table 3
Overall Precision Data For Alpha Alumina Determination

Mean Alpha Alumina Content %	r	R
< 10	0.7	1.0
>10	8% of mean	10% of mean

2.3 AS2879 Part 4 Determination of specific surface area by nitrogen adsorption

With this test being performed on many different commercial instruments, the method is designed as an optimal set of conditions rather than a prescriptive procedure.

In this method the sample is degassed for one hour at 150° C and then cooled in a bath of liquid nitrogen. The surface area is then determined by either a static or dynamic method.

In the static method the change in pressure or volume of the nitrogen is measured after the nitrogen is adsorbed by the sample. In the dynamic method the quantity of nitrogen adsorbed by the sample is measured by the changes in the thermal conductivity of a flowing mixture of nitrogen and inert carrier gas such as helium.

The test results are normalised against the sequential analysis of a carbon certified reference material. A number of laboratories use a degassing temperature of 300° C, but this is not recommended for all aluminas. Tests showed that this may cause loss of water from gibbsite present, resulting in increases in surface area of up to 5 m^2/g.

This standard will shortly be reviewed in the light of long term stability information received concerning the carbon reference standard.

Table 4
Precision Data For Specific Surface Area Determination

Specific surface area (m^2/g)	Repeatability r	Reproducibility R
43	1.3	1.8
51	1.3	1.3
58	2.5	2.6
62	1.6	2.3
72	2.8	3.0

2.4 AS2879 Part 5 Determination of Angle of Flow

The method is suitable for determining the angle of flow of smelter grade aluminas in the range of 30 deg to 50 deg . The angle of flow is the angle subtended by the side of the cone to the horizontal base of the container after alumina has flowed through an orifice in the base. Angle of flow is an indicator of the handling properties of the material. The sensitivity of this test to such parameters as vessel dimensions and hole size are discussed in detail elsewhere (T.Smith, 2nd Alumina Quality Workshop, Perth, 1990).

Table 5
Precision Data For Angle of Flow Determination

Mean Angle of Flow	Repeatability r	Reproducibility R
38.4	1.36	5.10
39.1	1.94	4.20
43.3	0.74	5.75
46.1	1.32	2.20
48.8	1.73	4.91

2.5 AS2879 Part 6 Determination of the mass distribution of particles sizes using electroformed sieves.

The issue of developing a sieving method has been on the MN/9 agenda since the inception of the committee. This was because particle size was considered to be a critical analysis, while at the same time inter-laboratory agreement was very poor. There were many obstacles to overcome in this work. The committee considered issues such as

- selection of sieve type
- optimisation of test portion
- shaking method and shaking time
- cleaning of sieves
- calibration of sieves

Initial efforts to standardise using wire woven sieves proved difficult. Some success was achieved by calibration against standard glass beads (NBS SRM 1004a). This procedure was, however, difficult and the long term availability of the beads was not assured.

More recently, high quality certified sieves constructed from precision electroformed screens have become available. Use of these sieves is the basis of the more straightforward and accurate method described in this standard.

The move to electroformed sieves was done for a number of reasons :

- the precision of results from these sieves was a major improvement over wire sieves
- the tolerances on the sieve aperture for these sieves was $\pm$ 2 micron (as tested by direct measurement optical methods)
- with these tight tolerances the need to calibrate with glass beads is eliminated
- the electroformed sieves are less susceptible to blinding
- the electroformed sieves are easier to clean

Table 6

Precision Data for Particle Sizing by Electroformed Sieves

Sample S-074	*+150 micron*	*+106 micron*	*+75 micron*	*+53 micron*	*+45 micron*
Mean	7.6	43.4	80.6	91.1	93.2
Std Dev	0.4	2.3	0.4	0.3	0.3

Sample S-075	*+150 micron*	*+106 micron*	*+75 micron*	*+53 micron*	*+45 micron*
Mean	18.5	59.2	85.4	91.6	92.9
Std Dev	0.9	2.5	0.2	0.2	0.2

Sample S-076	*+150 micron*	*+106 micron*	*+75 micron*	*+53 micron*	*+45 micron*
Mean	3.9	31.5	72.8	91.2	94.7
Std Dev	0.6	2.7	0.6	0.9	0.1

2.6 Part 7 Determination of trace elements - wavelength dispersive x-ray fluorescence spectrometric method

This standard specifies a method for analysing smelter grade alumina for a comprehensive range of trace impurities using a wavelength dispersive x-ray fluorescence spectrometer. The method is valid for any or all of the following elements: sodium, silicon, iron, calcium, titanium, phosphorous, vanadium, zinc, manganese, gallium, potassium, copper, chromium and nickel. The elements are expressed as the oxide and on an as-received basis. The applicable concentration ranges are as follows:

Component	Concentration Range %
Na_2O	0.10 to 1.00
SiO_2	0.005 to 0.050
Fe_2O_3	0.005 to 0.050
CaO	0.001 to 0.10
TiO_2	0.001 to 0.010
P_2O_5	0.001 to 0.050
V_2O_5	0.001 to 0.010
ZnO	0.001 to 0.010
MnO	0.001 to 0.010
Ga_2O_3	0.001 to 0.020
K_2O	0.001 to 0.010
CuO	0.001 to 0.010
Cr_2O_3	0.001 to 0.010
NiO	0.001 to 0.010

The x-ray fluorescence method was another method that was tabled for development in the early days of the MN/9 committee.

However it was not until the last four to five years that enough participants on the committee had access to an x-ray fluorescence spectrometer to enable extensive method development and relevant test programs to proceed.

The committee had to consider a large number of variables in this method

- pressed powders versus fusions
- range of elements to be analysed
- choice of fusion temperature and fusion time
- choice of fusion mixture and sample to flux ratio
- changes and improvements to x-ray fluorescence spectrometers in recent years

The method finally selected for a full test program involved the use of a mixed fusion mixture called 12:22 (lithium tetraborate and lithium metaborate) at 1100° C. The sample to flux ratio was initially set at 1:2 but with the improvements to x-ray fluorescence spectrometers in recent years it was shown that it was possible to use a sample to flux ratio of 1:5 without sacrificing precision.

The method takes into account common sources of error associated with the analysis of alumina eg. silicon contamination, interelement line overlaps and purity of base constituents. There has been particular care to set out a straight forward approach to designing accurate counting strategies for the required level of precision. As well an example of the calculations required for the changing of sample to flux ratio has been included.

Detailed round robins were carried out between all members of the committee to trial this method. In this round robin a number of different x-ray spectrometers were used from several different manufacturers. These included sequential spectrometers and a combination simultaneous/sequential spectrometer as well a sequential spectrometers with close coupled optics.

At the time of writing this paper the method is in the final draft form prior to being published as a standard in early 1996.

3.0 FUTURE AREAS OF WORK

3.1 Sampling

The development of this standard is in the early stages with two committee drafts having been produced and two detailed stopped belt trials versus auto samplers have been carried out. It is hoped that a Draft Standard will be available for comment within two years.

3.2 Bulk Density (Loose and Packed)

A recent round-robin amongst MN/9 committee members has highlighted the difference in methods currently used and the variability obtainable using the existing ISO 903 standard. Results available from a simple modified apparatus have shown substantially better precision with reduced sensitivity to variables present in the ISO method. Test work is underway using this apparatus to produce a standard.

3.3 Dustiness

The most recognised method of dustiness measurement has been on the Perra-Pulvimeter. This is a very specialised piece of equipment, and requires great skill and care in operation. The development of a standard based on this technique is considered to be impractical. A more robust technique based on the elutriation principle is under consideration. The results so far are encouraging and work is continuing.

3.4 Flow Funnel

Alumina flow properties have assumed greater importance in recent years especially with the advent of point feeders at smelters. Development of a standard has largely revolved around the merits and acceptance of various empirical tests, and the selection and testing of a final candidate. It is likely that finalising this standard will depend on the availability of standardised apparatus at enough sites for statistically valid testing.

3.5 Attrition Index

Like dustiness, Attrition Index is an empirical technique that is highly dependent on the apparatus and conditions used. In addition, current methods are cumbersome and require considerable skill and care in operation. The development of a more robust method which will give results comparable to the more traditional method is in progress with two pieces of apparatus being trialed at the moment.

3.6 Methods of Sample Preparation and Handling

Recent work has highlighted the need to closely examine methods for the handling (or "equilibration") of alumina prior to analysis. Equilibration effects many physical tests such as bulk density, loss on ignition, flow funnel time, attrition index and dustiness.

A sample preparation standard is being developed which will help to improve the precision of previously published standards. It will also be incorporated in future standards published.

3.7 Review of Loss of Mass on Ignition Standard

Standards Australia procedures require the review of previously published standards after a set period of time. With this in mind the committee is now reviewing AS 2879- Part 1 (1986) Determination of Loss of Mass at 300° C and 1000° C. When this standard was published the precision obtainable from instrumental techniques was considered to variable to be considered. However these instruments have now improved significantly and a test program is currently underway to look at including instrumental

techniques in this standard. Initial testwork on modern instruments have given exceptionally good results.

4.0 CONCLUSION

The standards published by this committee are in response to the recognised need in the early 1980's for high quality standard methods for the analysis of Smelter Grade Alumina. These standards now cover a considerable range of the necessary properties for the certification of alumina quality, however there remains a large amount of work especially in the area of physical analysis (flow funnel, dustiness, attrition index and sampling).

All standards have been subjected to rigorous technical scrutiny and exhaustive testing, and publicly reviewed before publication. They include statistical data on performance, and a wealth of technical and procedural information for the analyst. All methods are subject to triennial review, and are updated as appropriate based on user feedback and changes to technology.

To date the input to these reviews has primarily been from within Australia. It is desirable that international users participate in the review process, so as to contribute to the continuing improvement of the standards and their international acceptance.

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