— Light Metals —

ALUMINIUM CLEANLINESS MONITORING:  METHODS AND

APPLICATIONS IN PROCESS DEVELOPMENT AND QUALITY CONTROL

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## Summary

   The control of metal cleanliness is an essential part of the production of critical alloys.  The measurement of metal cleanliness is complicated by the nonuniformity of the distribution of nonmetallic inclusions and by the extremely low concentrations encountered in most wrought aluminium alloys.

   This report describes the methods currently used by Alcan companies for the measurement and control of metal cleanliness.  Examples of the effect of various melt treatment practices on metal cleanliness are given.  Recent advances in the development of rapid, in-line methods of cleanliness assessment are reviewed.

## Introduction

   The detrimental effects arising from the presence of nonmetallic inclusions in aluminium are well known.  These include, for example, pinholes in light gauge foil, flange cracks in beverage containers and surface streaks in bright automotive trim.  A substantial number of methods are used in the cast-house in order to remove inclusions from the melt either prior to or during casting.  Furnace fluxing in combination with settling is probably the most ubiquitous technique and, as will be shown later, can be very effective, removing a substantial proportion of inclusions larger than about 20 μm in diameter.  In addition, the last decade has seen the introduction of a number of in-line treatment systems most of which are designed to reduce the concentration of inclusions either alone or in conjunction with hydrogen or alkali metal removal.

   Despite the substantial efforts of a large number of individuals our knowledge of the efficiency of inclusion removal techniques has been severely limited by the lack of a sensitive, quantitative method of measuring metal cleanliness and much of the progress achieved to date has proceeded on a more or less empirical basis using product performance as the sole or chief measurement criteria.

   With the increasing tendency towards thinner gauge products and more stringent customer requirements concerning surface finish, etc., there is a pressing need for a sensitive and rapid means of assessing metal cleanliness.  The goal of the present paper is to outline some of the approaches to the problem of measuring metal cleanliness that have been used and investigated by Alcan.  Where appropriate, references to published work in this area by other organizations have been included.

## Background

   The term "inclusion" requires definition.  For the purposes of the present paper it can be taken to mean "any exogenous solid or liquid phase present in aluminium above the liquidus temperature".  Thus titanium diboride ($TiB_2$) is considered to be an inclusion whereas $TiAl_3$, which under conditions normally encountered in the industry is soluble, is not.  Likewise liquid salt droplets arising either from solid flux additions or chlorine fluxing are considered to be inclusions whereas gas bubbles are not.

   The size at which an inclusion becomes potentially troublesome varies of course with the end-use application.  In general, in critical applications, we consider any  inclusion larger than 10-20 μm in diameter to be deleterious although even smaller inclusions can cause problems if present in sufficient quantity.

   It must be stressed at the outset that the analysis of inclusions is, in most cases, trace analysis.  Figure 1 shows the number of inclusions per kg of metal required to produce the indicated volume fraction as a function of inclusion diameter.  It can be seen that, even for large inclusions (d = 50 μm) enormous numbers are required to produce volume fractions approaching the part per million level.  We have found that the volume fraction of inclusions (d > 20 μm) present in fluxed and filtered metal typically ranges from 5 to 50 parts per billion.

   The preceding  observations have tremendous implications on the sensitivity required of any analytical technique whose purpose is to quantify metal cleanliness.
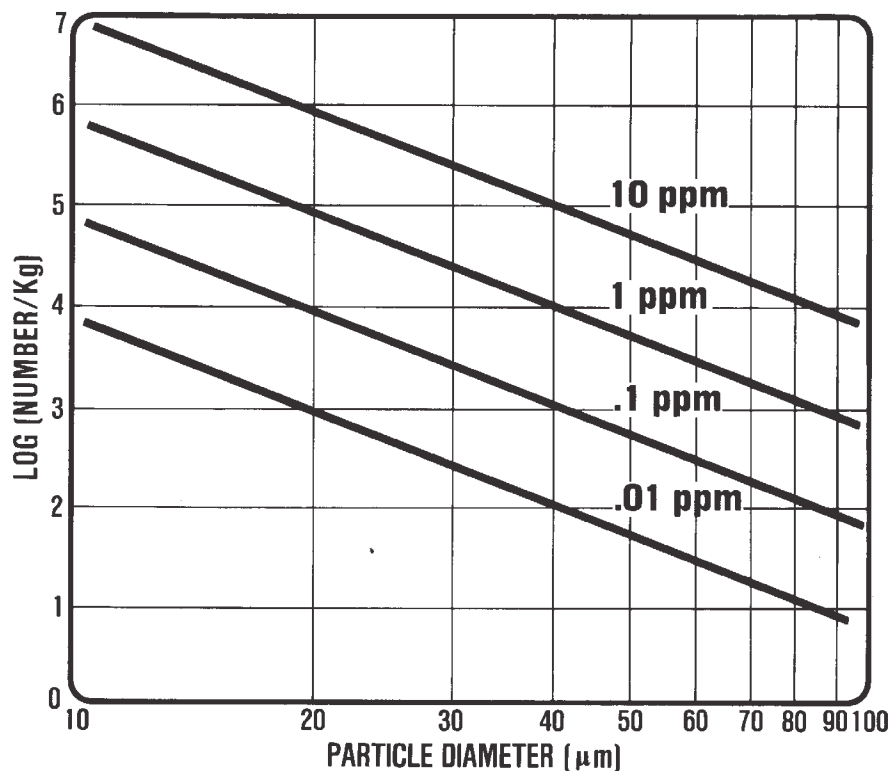
Figure 1 - Inclusion Concentration Required to
Produce the Indicated Volume Fraction as a
Function of Particle Diameter.

Apart from mid and end-product performance results, there remain essentially three major approaches to the problem of measuring metal cleanliness.

    I   Chemical Analysis
   II  Metallographic Evaluation
  III  Techniques based upon physical principles.

In general, chemical and metallographic methods necessarily entail a substantial time delay between sampling and obtaining the report of analysis. Much effort has been focussed recently on the development of techniques based on physical principles. These, at least in principle, can provide results rapidly and thus allow the possibility of real-time process control.

I.   Chemical Methods

Attempts at direct wet chemical or instrumental analysis of inclusions in aluminium have met with very limited success. This is due, in large measure to the very low concentration at which inclusions occur, their

nonuniform distribution and to the fact that the measurement of the bulk concentration of an element or compounds reveals nothing about how it is distributed within the sample. For example, it has been determined that there is no correlation between the oxygen concentration (determined by neutron activation analysis) and the inclusion level (d > 20 µm) in the melt. Typical oxygen levels in aluminium range between 5 to 50 ppm with most of this present either in the surface oxide or in submicron sized films. Any additional oxygen present due to the presence of inclusions cannot be distinguished above the large and variable background oxygen levels.

Selective dissolution of the aluminium matrix followed by gravimetric determination of the residue has been reported by Levy et al (1). Their results showed a wide degree of scatter in duplicate samples and no correlation was found between the mass of the residue and metal processing (filtration). Attempts at Alcan to analyze extraction residues by means of a Coulter counter revealed that there was no correlation between the results obtained and those provided by a metallographic technique. It was concluded that the quantity of artifacts generated as a result of the dissolution steps completely overwhelm the actual inclusion concentration present in-situ in the metal. A similar approach has also been reported by Siemensen (2, 3).

The determination of carbides by gas chromatography has been reported by Siemensen (4) and, while this technique has found some use in certain specialized applications involving carbide removal (5), the method falls far short of, and was never intended to be a practical method of assessing overall melt cleanliness.

II.  Metallographic Methods

The most obvious method of assessing the inclusion content of aluminium is undoubtedly the direct examination of polished sections. However, as anyone who has ever examined a macrosection of a DC cast ingot can attest, some method of preconcentration is required in order to observe any significant number of inclusions within a reasonable area.

Following the work of Cibula (6), preconcentration of inclusions by centrifugation was investigated at Alcan in the early 1950's. More recently, reports of this approach have appeared by Mollard et al (7) and by Siemensen (2). The necessity that the samples be remelted with the consequent potential for oxidation and particle agglomeration cast doubt upon the validity of this technique. Although this problem could have been overcome by installing the centrifuge in the casting area the decision was made to adopt the mechanically simpler approach of pressure filtration.

Preconcentration of inclusions by filtration has been reported by a number of authors (8, 9, 10) and undoubtedly most of the major producers have employed this approach. Alcan's experience in this domain dates back to 1960 and has standardized this method, referred to as PoDFA (Porous Disc Filtration Apparatus) for use in sampling all of its critical (inclusion sensitive) products. Figure 2 outlines the principle of the test. By rigidly standardizing all aspects of materials and procedures it has been possible to reduce the variability of the results to the extent that the quantity (area) of residue present on the filter disc can be used to set release criteria for critical products. The technique can also distinguish inclusion type and differentiate for instance between the level of borides, carbides and spinels present within an individual sample. This latter, qualitative, aspect of the technique has proved invaluable in establishing the cause of the problem in unsatisfactory metal. Figure 3 shows an application of the PoDFA technique
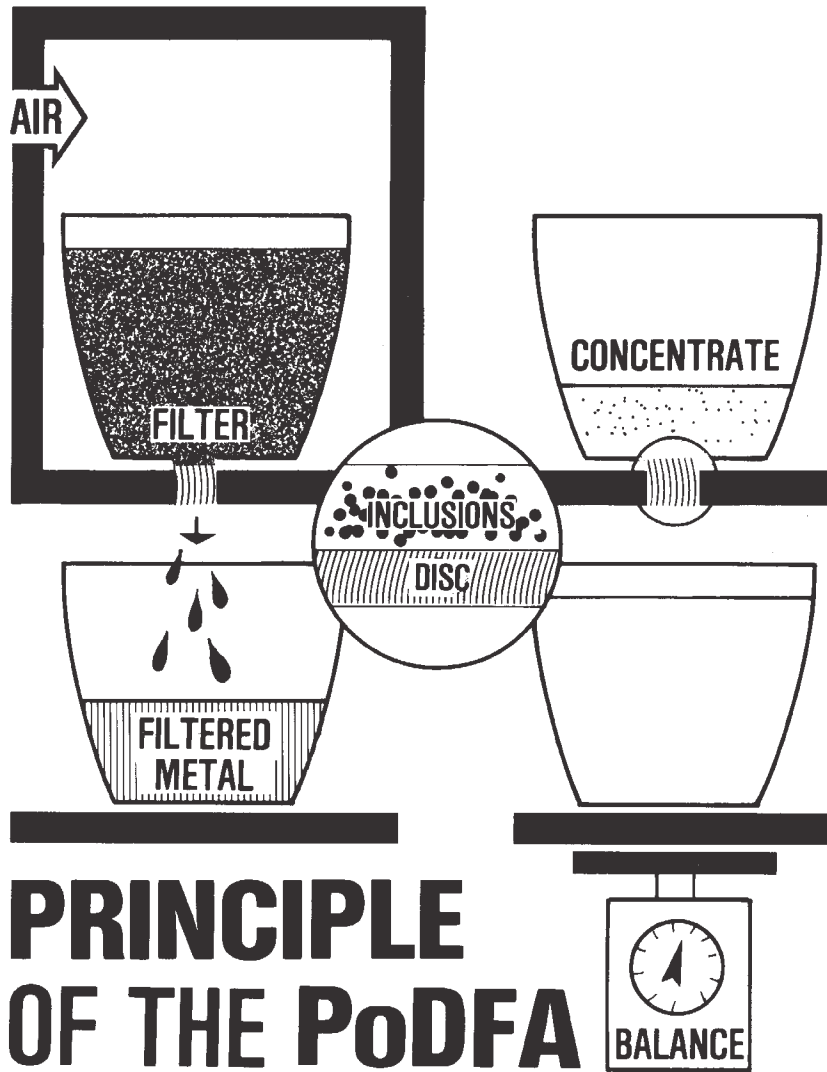
Figure 2 – Principle of the PoDFA
(Porous Disc Filtration Apparatus)
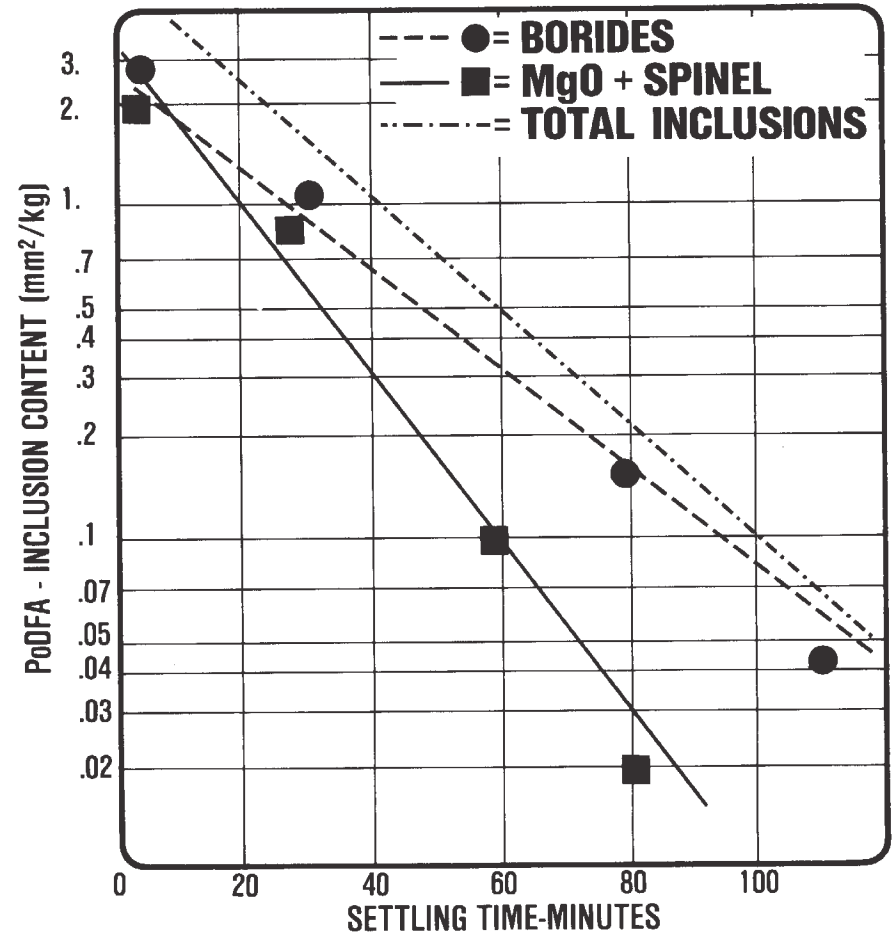Method of Measuring Metal Cleanliness.



Figure 3 – Effect of Settling Time on the
Inclusion Concentration Measured by the
PoDFA Technique.

to the investigation of the effect of settling time on the inclusion content within a reverberatory furnace.

The PoDFA technique has also been used to evaluate the performance of in-line melt treatment devices. Figure 4 shows the effect of using two different gas mixtures ($N_2$, 0.6% $Cl_2$ and Ar, 0.6% $Cl_2$) in a commercially available in-line degassing device. The results indicate that the use of a nitrogen based fluxing gas leads to a decrease in melt cleanliness as the metal passes through the unit whereas when argon was used there was no significant change in metal cleanliness. Examination of the inclusion concentrates obtained after the unit while using nitrogen revealed the presence of large numbers of oxide films which were absent in samples taken before the unit or while the unit was operated using argon.
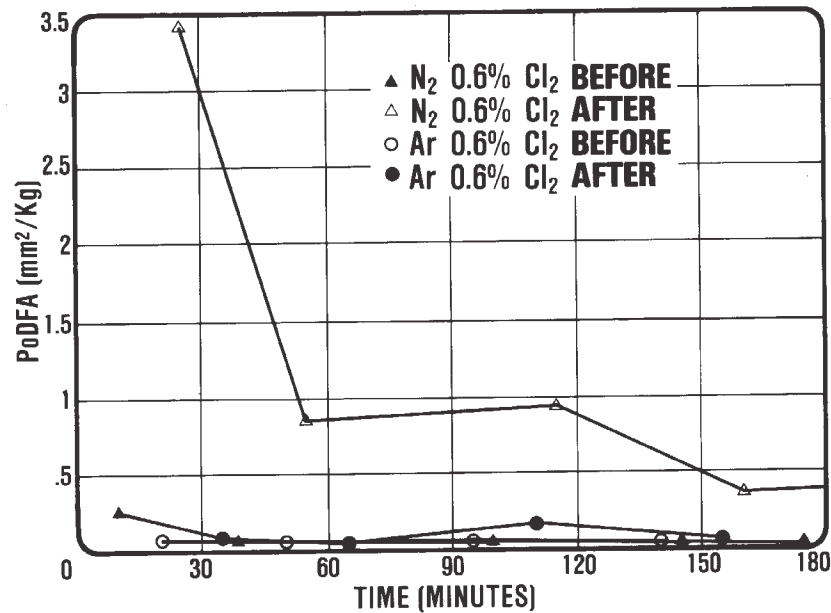
were ultimately compared to the result of the metallographic evaluation of the inclusion concentrate.

Typical mass-time curves and the corresponding inclusion areas are shown in Figure 5. It can be seen that, while extremely dirty metal (> 1 $mm^2$/kg) can be distinguished from clean metal, the technique provides no resolution in the range of interest (0 to 1 $mm^2$/kg). The results provided by this technique were found to reflect the level of small (< 5 μm) particles (i.e. grain refiner nuclei, carbides) and were unaffected by the much lower concentrations of larger, more harmful inclusions. A similar approach was adopted by Levy (9) using a modified Union Carbide Particulate Tester; unfortunately the results of replicate samples were not presented.
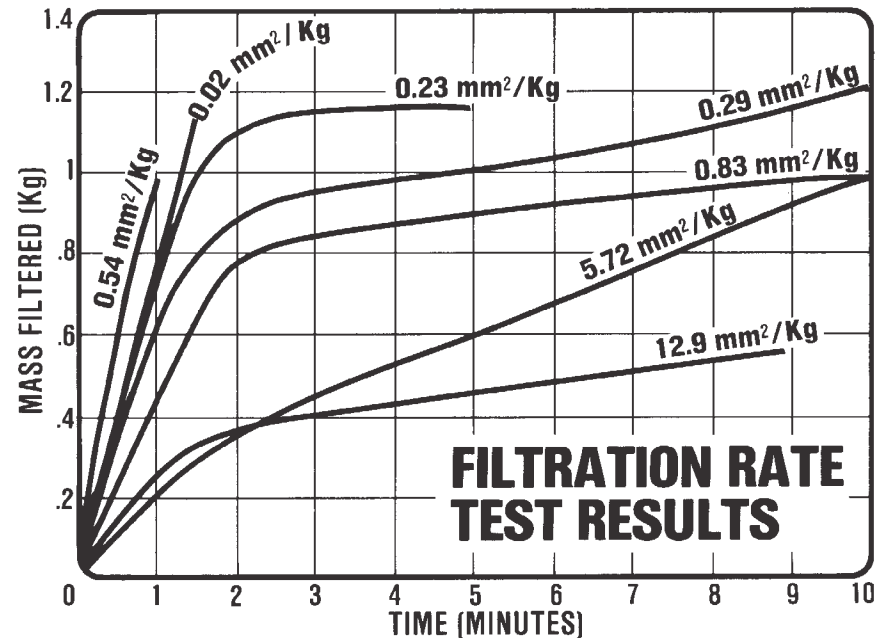


Figure 4 — Effect of Gas Composition
on the Performance of an In-Line
Melt Treatment Device.



Figure 5 — Filtration Rate Test Results:
Mass-Time Curves and the Corresponding
Areas of the Inclusion Concentrate.

III. In-Line/Physical Methods

a) Filtration Rate Testing

Filtration rate testing was examined as a potential method of metal cleanliness assessment. This involved recording the weight/time curve while providing continuous metal temperature measurement and control. Using a microprocessor, mass/time/temperature curves were recorded during PoDFA analysis and attempts were made to extract meaningful curve-fitting parameters which

b) Ultrasonic Testing

Several reports of the application of ultrasonic inspection of molten metal have been published in the last few years, notably by T.L. Mansfield (11, 12, 13). Alcan's experience in applying ultrasonic techniques in molten metal dates back to the mid 1960's when an apparatus capable of attenuation and discontinuity measurements built and used to obtain measurements both in transfer launders and directly in reverberatory furnaces (Figure 6). Even in
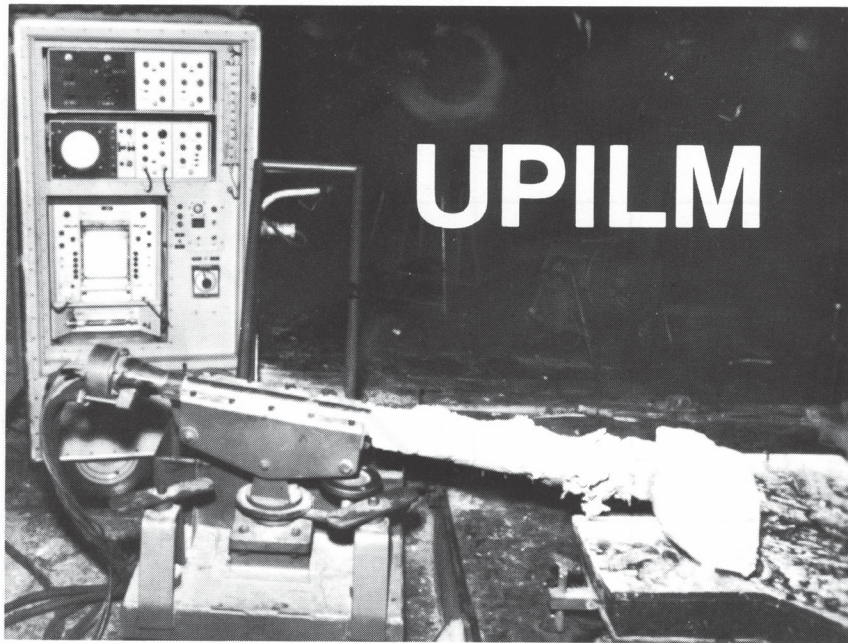
Figure 6 – Ultrasonic Evaluation of
Molten Metal Cleanliness, 1964.



Figure 7 – Ultrasonic Attenuation of Molten Aluminium
Before and After Filtration.

intentionally dirtied metal, discontinuity measurements were very low, an
observation presumably reflecting the low resolving power of the technique
(according to the "λ/2" criterion the detection limit for an individual in-
clusion or cluster in aluminium for this type of measurement is above 200 µm
using an excitation frequency of 10 MHz).

Attenuation measurements were somewhat more successful and the
effect of, for instance, filtration was evidenced by a decrease in the ultra-
sonic attenuation (Figure 7). This instrument used a two-probe sender/
receiver unit and required external calibration before each use. Consid-
erable practical problems had to be overcome in order to maintain probe
alignment and ensure uniform wetting of the titanium wave guides. Extensive
sampling in conjunction with the PoDFA technique showed that extremely clean
metal could be distinguished from extremely dirty metal but that the reso-
lution at intermediate cleanliness levels was limited (Figure 8).

These limitations, in conjunction with the inability of the techni-
que to provide particle size distribution data finally led to its abandon-
ment in the early 1980's in favour of a new approach that will be described
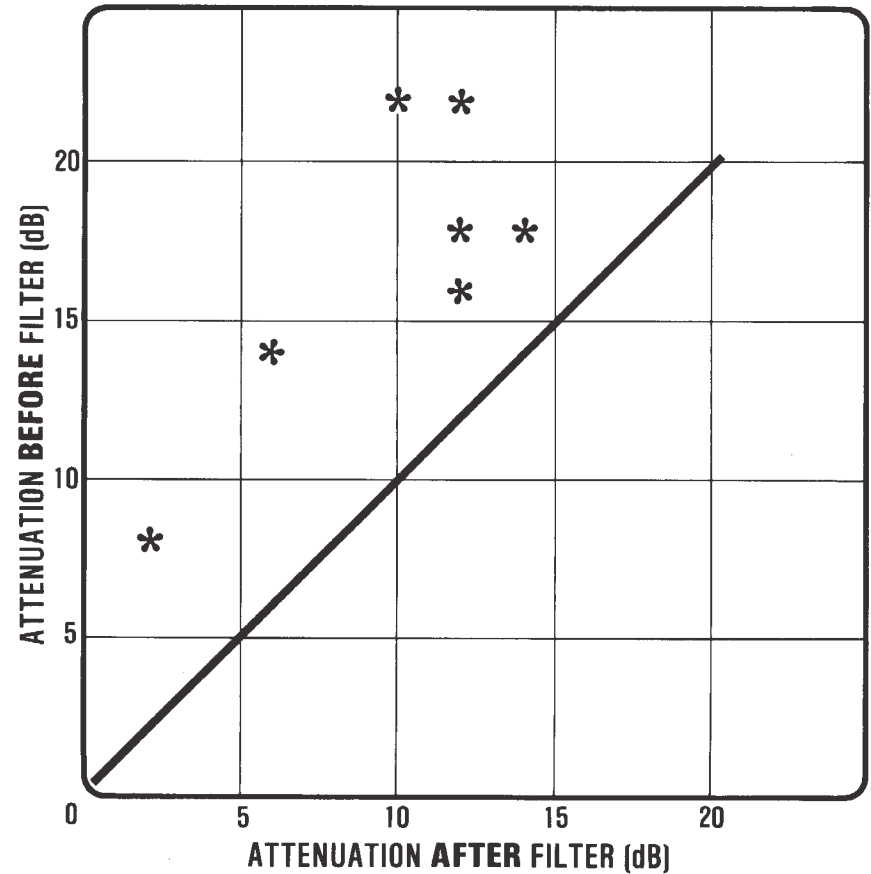next.

Figure 8 – Ultrasonic Attenuation Versus
Pressure Filtration (PoDFA) Results.

## Electrical Properties

Recently, work was begun in collaboration with McGill University on a completely new approach to the problem of assessing metal cleanliness. The goal was to develop a rapid method capable of providing both the concentration and the size distribution of inclusions larger than 15 to 20 $\mu$m (0.6 to 0.8 x $10^{-3}$ inches). The technique is based upon measuring the electrical properties of a thin liquid metal stream. Transient changes in these properties occur when any large inclusion is present in the stream.

Counting the number of such changes per unit volume of metal samples provides a measure of the overall inclusion concentration while recording the amplitude of each allows the particle size distribution of the inclusions to be deduced. Thus the technique can provide both concentration and particle size distribution data simultaneously.

Prototype models have been built and used to measure metal cleanliness in a number of Alcan casting centres. Sampling is carried out directly in the transfer trough and the results of the analysis are available at approximately two-minute intervals. Using this technique, it is possible to take up to 40 samples during a typical drop and to investigate the time dependency of metal cleanliness.

Table I shows an example of the application of the method to investigate the precipitation and settlement of titanium-vanadium borides. These are formed as a result of the addition of boron containing master alloys to smelter grade metal in order to reduce electrical resistivity. Commercial grade aluminium (99.7%) was melted and held in a resistance furnace for six hours (A). The melt was stirred (B), settled for two hours (C) and treated with a 20 ppm w/w addition of boron stirred into the melt (D). Following subsequent stages of settling and stirring (E through I) a second addition (85 ppm w/w) of boron was made (J) followed by a final period of settling and stirring (K-M). All transients corresponding to particles of at least 20 $\mu$m in equivalent spherical diameter (d) were recorded. Metallographic examination of chill plates taken after the boron additions subsequently confirmed the presence of (Ti-V) $B_2$ particles in the predicted size range (20 to 50 $\mu$m).

Table I. Effect of Boron Additions, Settling and
Stirring on the Cleanliness of Commercial Grade Aluminium

| | PROCESS OPERATIONS | CONCENTRATION OF INCLUSIONS (d > 20 $\mu$m) per kg |
|---|---|---|
| A | Metal held at 700$^{\circ}$C for 6 hours | 850 |
| B | Melt stirred | 8,200 |
| C | A 2 h settling period allowed | 2,900 |
| D | A 20 ppm addition of boron stirred into melt | 74,000 |
| E | Following a 5 minute settling period | 23,000 |
| F | Melt stirred | 75,000 |
| G | Following a 50 minute settling period | 20,000 |
| H | Following a 1 hour, ten minute period | 8,400 |
| I | Following a further 1 hour, ten minute period | 8,000 |
| J | An 85 ppm addition of boron stirred into melt | 227,000 |
| K | Following a 10 minute settling period | 95,000 |
| L | Following an overnight ($\sim$ 12 h) settling period | 2,100 |
| M | Melt stirred | 74,000 |

In order to confirm that these effects also occur on an industrial scale, measurements were taken at a centre producing E.C. grade wire by the Properzi process. Figure 9 shows the results obtained on two batches of metal, one of which had received the allotted settling period (lower curve) and the other which had been intentionally stirred just prior to the start of casting (upper curve). The effectiveness of settling as a means of avoiding the presence of particles larger than 20 μm is obvious. It was also found that the settling curve for this population of particles could be represented by a simple exponential function:

$$C(t) = C(o)\, e^{-kt}$$

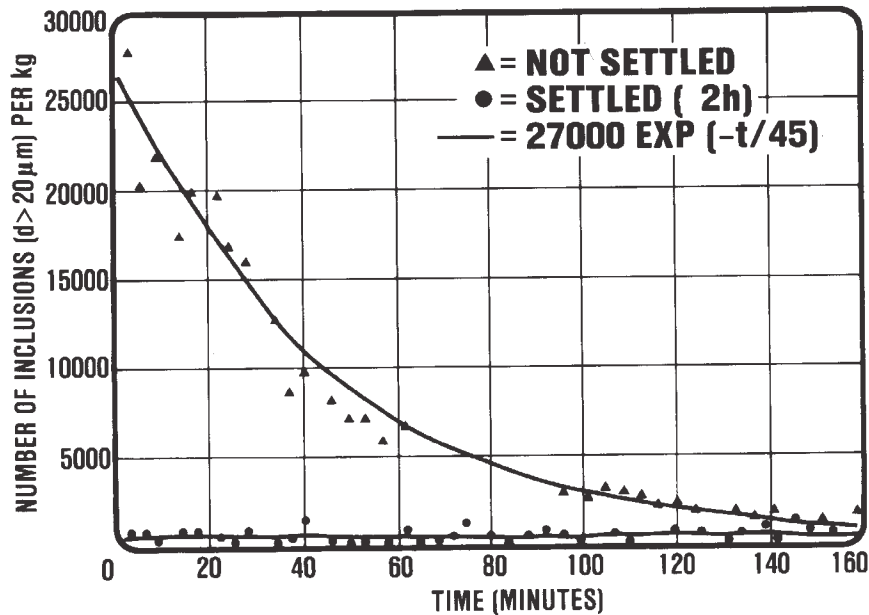with a "lifetime" ($t = {}^{1}/k$) of approximately 45 minutes.



Figure 9 – Effect of Settling on the Concentration of Inclusions Larger Than 20 μm During the Production of Boron-Treated E.C. Grade Aluminium.
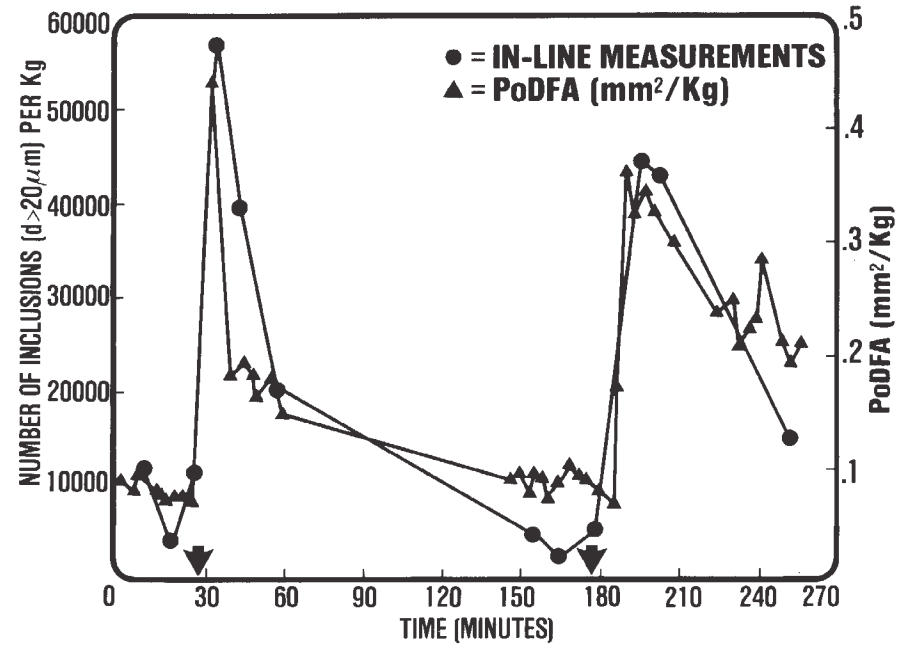


Figure 10 – In-Line Electrical Measurements and Pressure Filtration (PoDFA) Results Versus Time. Arrows Indicate Times at Which the Furnace Feeding the Caster was Changed.
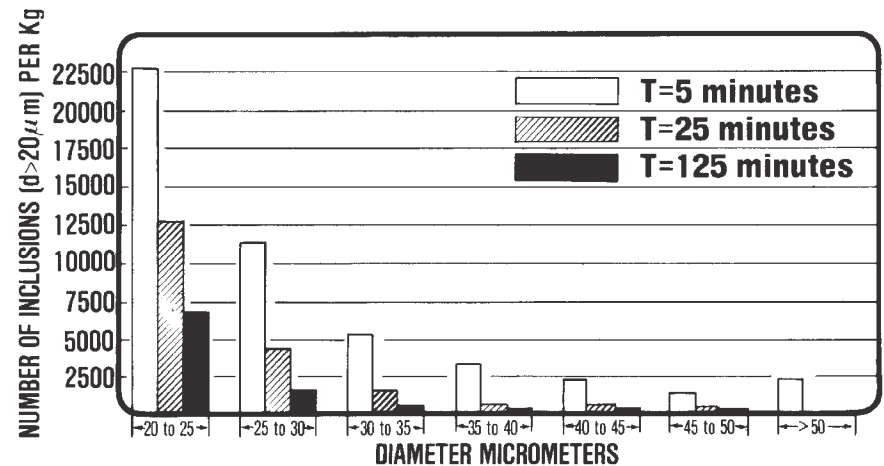


Figure 11 – Particle Size Distributions Provided by the In-Line Electrical Measurements 5, 25 and 125 Minutes After the First Furnace Change Indicated in Figure 10.
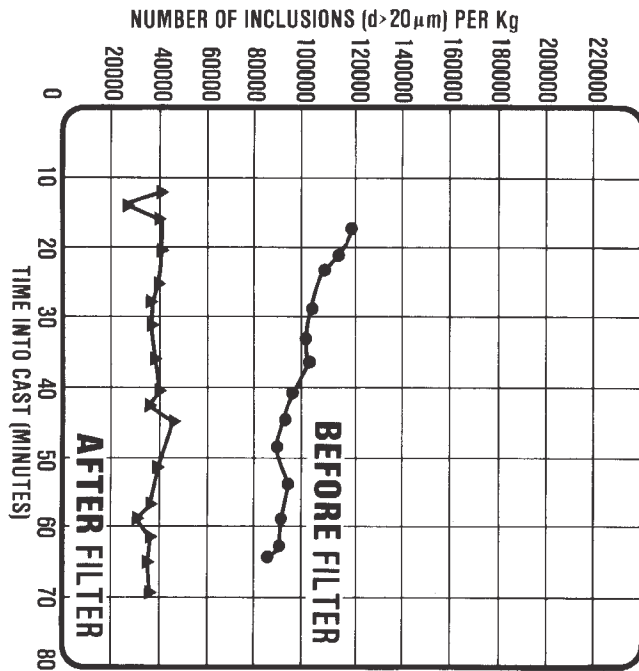
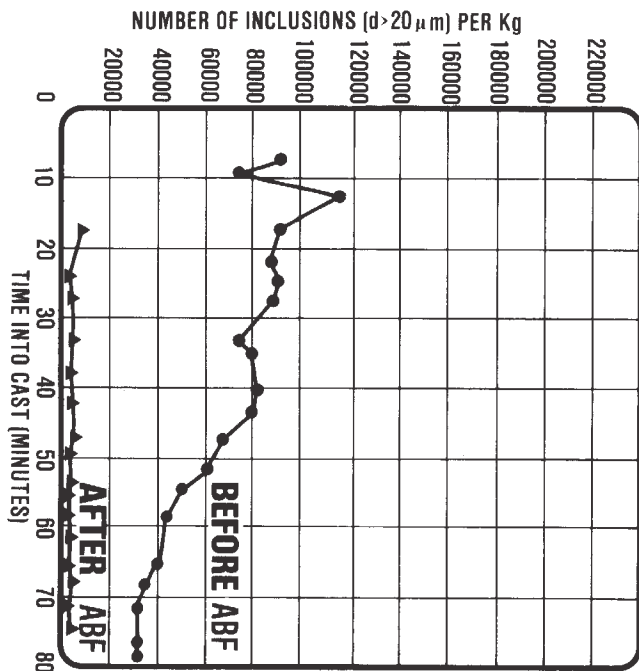Figure 12 – Concentration of Inclusions (d > 20 µm) Before and After Filtration Through a Single-Use Filter.



Figure 13 – Concentration of Inclusions (d > 20 µm) Before and After Filtration Through a Graded Bed Filter (Alcan Bed Filter).

The results have also been shown to be in good agreement with those obtained using the PoDFA (pressure filtration) technique. Figure 10 shows the results obtained while conducting parallel sampling using both techniques. In this location several reverberatory furnaces are used to provide an uninterrupted metal feed to a continuous caster. It can be seen that when furnace changeover occurs there is an abrupt increase in the level of suspended inclusions followed by a decline. Figure 11 shows the particle size distributions obtained from samples taken 5, 25 and 125 minutes after the first furnace changeover. It is clear that not only are the larger inclusions settling faster than the smaller ones but also that a significant portion of the smallest inclusions measured (20-25 µm) is removed due to settling.

As a final example, Figures 12 and 13 show a comparative evaluation of the efficiencies of a commercially available single-use filter with that of a deep-bed type of filter (Alcan Bed Filter). Extensive in-plant testing of both filter systems has shown that the removal efficiency* for particles larger than 20 µm of the former is typically 30 to 60% whereas that of the latter is typically greater than 90%. These results were obtained at a single casting centre while producing the same alloy.

These examples also serve to illustrate the sensitivity of the technique. For instance, in the case of metal that has passed through the bed filter, there are typically 500 to 1000 inclusions larger than 20 µm per kg of metal. On a volume fraction basis this corresponds to roughly 10 to 20 ppb (parts per billion).

### Conclusions

Over the years Alcan has investigated a wide variety of methods for the assessment of metal cleanliness. Until very recently none of the available techniques could provide results with the sensitivity, speed and precision required in order to allow real time process monitoring. New developments reported herein appear to satisfy this need and, in combination with the PoDFA technique have allowed us to achieve considerable quantitative insight into some of the factors that influence metal cleanliness.

### Acknowledgements

*Removal efficiency =

$$\frac{\text{inclusion concentration (d >20 µm) before} - \text{inclusion concentration after}}{\text{inclusion concentration before}}$$

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