

MANAGEMENT OF IMPURITIES IN CAST HOUSE WITH PARTICULAR REFERENCE TO Ni AND V

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Abstract

It is apparent that the concentrations of impurities in raw materials (particularly petroleum coke) are increasing with significant implications for the ability of cast houses to meet customer chemical specifications. A large fraction of the metal content (Ni, V) of the coke and alumina (Fe, Si, Ga, Zn) reports to the Al in the reduction cells. In some smelters the concentration of these impurities is beginning to exceed customer cast product specifications. These impurities can have detrimental effects in certain alloys. In order to formulate control strategies, this paper reviews process options including the classical melt treatment processes of salt fluxing, degassing and filtration for removing impurities in the cast shop. The mechanism of Al boride treatment to remove titanium, chromium, vanadium is examined to get a picture of the possibility of speeding up the process. Those processes used for producing super purity Al are also examined along with refining methods in other non-ferrous metals for potential application to Ni and V control. An investigation into potential for a melt nickel removal process is recapped. We conclude that currently cast house cannot provide a complete solution to the issue of Ni and V control.

Introduction

Impurity issues in primary Al smelting have historically been centered around the control of particles and dissolved hydrogen and alkali earth metals. However, an emerging issue is the increase in certain impurities (Ni and V) due to changes in raw materials (anode coke) composition profiles [1, 2]. The impurity issues in secondary smelting have a different focus. For example there is a mismatch between the available alloy mix of scrap inputs and the desired products to be made. Wrought alloy makes most of the input while Al-Si foundry alloy is the majority of product. This situation leads to an excess of magnesium. There is also problem associated with the pick-up of trace elements in the scrap handling system, particularly Fe but also Pb and Ca.

In this paper the classical Al melt treatment processes of salt fluxing, degassing and filtration used to remove alkali metals and solid particles are reviewed. Al boride treatment for removal of V and Ti and processes used for producing super purity Al are also described. General refining processes used in other non-ferrous metals are also examined for applicability to Al.

Stages and Methods of Cast House Impurity Control

Current cast house refining processes were extensively reviewed by Zhang *et al.* [3], Le Brun [4], Grandfield *et al.* [5] and the fundamentals of these processes covered by Engh [6]. Refining options from a secondary perspective were also recently reviewed

by Gaustad *et al.* [7]. Our intent in this paper is to consider in particular where the technology opportunities may lie that can be applied to the issue of Ni and V control.

A common approach is to order the description of the current impurity removal and refining steps according to their stage in the process chain (as shown in **Figure 1**). They may also be described in terms of operating principle, e.g.

- Reaction with added solids
- Reaction with or evaporation into a purging gas
- Physical separation, such as filtration
- Particle flotation or settling

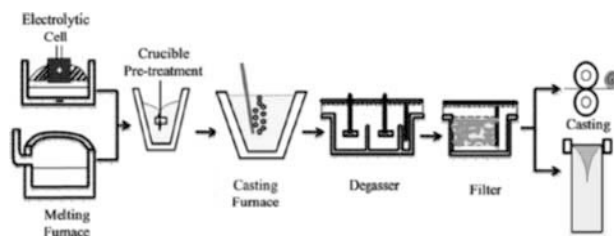


Figure 1 - Process chain in primary smelter showing impurity treatment steps from Waite [8].

In principle, any methods can be applied at any stage of the process, however, it makes more sense to carry out certain activities at different stages. For example, early removal of hydrogen would risk hydrogen pick up before casting during metal transfer operations. Certain operations such as settling are more effective in the furnace where the bath depth is shallower. Filtration works best in a continuous in-line configuration than in the furnace. The following sub-sections describe in more details the common methods and treatments for control and removal of impurities within the cast house.

Transfer crucible treatment

At present, the main driver for treatment in the transfer crucibles is the removal of Na and Li (when present) when alloy products with Na specifications (as low as 1 ppm) are produced from primary smelter metal typically containing 150ppm Na. As a consequence crucible treatment for control of other impurities is not done, however there is no reason why for example Al boride additions could not be made in the crucible.

Na in solution can be reacted with AlF_3 or $MgCl_2$ to produce a sodium salt that is then removed. Na also evaporates from the melt at all stages of processing, but because Na increases Al melt oxidation rates and dross generation, there is a financial incentive to remove Na as soon as possible after tapping [9, 10]. Crucible treatment systems (TACTTM and RAMTM are the two commercial

systems available) lower a rotor into the melt and AlF_3 is added either in Ar carrier gas (RAM) or as a powder (TAC). Although it could be added to the crucible, MgCl_2 is generally used in the holding furnace to remove sodium.

Al fluoride (AlF_3) in a filter bed format to remove sodium and calcium is also a possibility [11], but extension of this work to a commercial application has not been reported. In a similar way, a bed of Al boride might be used to remove V in order to reduce furnace cycle times.

In furnace refining

Degassing. Due to exposure to the atmosphere, Al melt quickly equilibrates with air and water vapour in the atmosphere resulting in saturation of hydrogen within the Al melt. Due to the solid solubility is much lower than the liquid solubility, porosity forms during casting if the hydrogen is not reduced to <0.2 ppm or in some cases <0.1 ppm. Hydrogen is easily removed by degassing into a carrier gas, typically argon or nitrogen. These degassing operations can take place in the furnace but are more commonly performed in in-line degassing units. Since neither dissolved V nor Ni have a high enough vapour pressure in Al this type of gas purge approach is not suitable for their control.

Sodium removal. Because of the health and safety hazards associated with the traditional chlorine gas fluxing [12], the industry has moved towards addition of MgCl_2 containing fluxes to remove sodium in the furnace. The resulting NaCl_2 is skimmed off with the Al dross.

De-Magging. In secondary operations, magnesium is still removed by chlorine fluxing to form MgCl_2 [13]. The dangers of chlorine have prompted examination of alternate methods such as addition of AlF_3 or SiO_2 which then reacts to produce MgO [14]. Addition of a gaseous reactant to remove V may be possible but examination of systems involving Ni has not identified a suitable system to date.

Boride treatment

Many of the inclusions in the melt are heavier than liquid Al and settle to the bottom of the furnace [15] allowing the purer liquid to be cast without them. This is the case with vanadium borides produced from AlB addition, which is commonly called boride treatment.

This treatment is applied to produce Al for application in electrical conductor such as for overhead power transmission cables. Smelter grade Al cannot be used as directly for electrical conductors due to higher concentration of transition metal impurities of V, Ti, Zr and Cr. These metal impurities in the form of solution in Al deteriorate the electrical conductivity significantly [16]. Industrially, boride treatment is carried out in a holding furnace where Al-B master alloys, containing either AlB_{12} or AlB_2 , are added into molten Al in the form of waffles, rods or wires.

It has been shown from thermodynamic study that solute V, Ti and Zr can react with B to form VB_2 , TiB_2 and ZrB_2 ; and that ZrB_2 is more stable compared to TiB_2 , VB_2 and AlB_2 [17]. It has also been shown that excess boron is required for high removal of the transition elements [18]. **Figure 2** shows, the thermodynamic prediction of the change in V, VB_2 and AlB_2 concentrations with temperature in the Al-1wt%V melt, in equilibrium with

stoichiometric and 75% excess B. It can be seen clearly that in the case of excess boron addition, a low V concentration in the melt can be achieved in the temperature range studied. While in the case of stoichiometric boron addition, V concentration increases with increasing temperature due to re-dissolution of VB_2 in the melt.

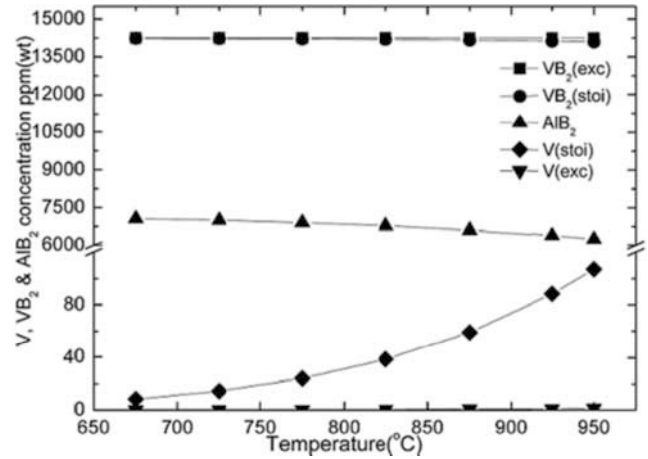


Figure 2 - V, VB_2 and AlB_2 equilibrium concentrations in Al-1wt%V melt in equilibrium with stoichiometric and excess B addition [18]

An experimental study carried out by Khaliq *et al.* [18] suggests that reaction between V and Zr with B takes place early after boride addition into the melt. The results from microstructure analysis show the formation of borides ring encapsulating the initial boron source (e.g. the AlB_{12} particles). An example of such ring in the case of reaction between V and B (AlB_{12}) is shown in **Figure 3**. It can be seen from **Figure 3** that reaction takes place at the periphery of AlB_{12} particles. Cluster of these particles, encapsulated by solid VB_2 layer, are then formed. These clusters of borides particles have high densities compared to Al melt and settle at the bottom of the furnace.

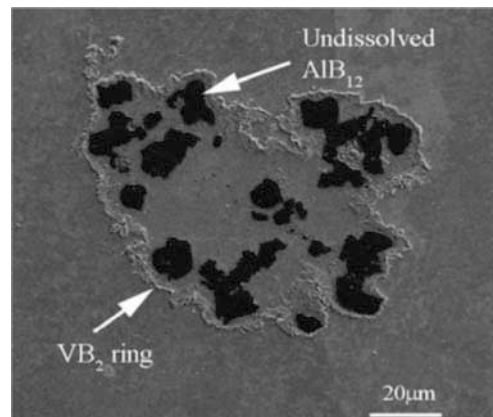


Figure 3 - A secondary electron SEM image of a cross section of borides clusters in the Al-1wt%V-0.412wt%B held at 750°C for 60 minutes [18]

The presence of these rings inhibits further reaction between V and B, therefore, there is a potential to improve the process by avoiding or disrupting the formation of these rings. Although boride treatment is commonly used in cast house to remove V, Zr,

Ti transition metals, further work to understand the detailed mechanism of the borides formation is still required to improve the efficiency and economy of the process.

A problem with the universal adoption of AIB treatment as a V control measure for all alloys is that the Ti is a desirable addition in many of them. Extra Ti addition would be needed to make up for the lost Ti thus increasing costs, i.e. in the order of \$5/t. The cycle time for boride treatment is of the order of an hour and will reduce throughput if applied to all products.

In-line gas or flux injection

There exists a plethora of gas purging in-line treatment systems with different gas delivery systems and configurations [4]. There has been considerable development of in-line treatment systems including

- Understanding of particle flotation by gas bubbles
- Improvement of gas bubble distribution to reduce gas usage and improve efficiencies
- Adding reactive fluxes such as $MgCl_2$

However, these systems are only applicable to Ni and V if a reaction product can be created or if they were in a particulate or volatile form.

In-line filtration

In-line filtration systems take a variety of forms; ceramic foam filter (CFF) tiles, rigid media filter (RMF) and deep bed filter. The inclusion capture mechanisms and operations of CFF filters [19-22] and RMF [23-26] have been extensively studied and their performance improved however they are only applicable if the Ni or V is in particulate form. Additionally, current filtration systems handle inclusion concentrations of the order of 1ppm or less. If they were presented with say 300 ppm of vanadium borides they would block up.

Techniques for High Purity Al Production

The properties of ultrapure Al include excellent corrosion resistance, relatively soft with high ductility, easy workability and low rate of work hardening, high thermal and electrical conductivity, and high reflectivity; making it suitable for certain niche applications such as capacitor foil.

There are a number of methods and techniques that can be used to refine and produce ultrapure Al; these include the three-layer electrolytic refining, zone refining (directional solidification), fractional solidification and their combinations. Due to their high cost, these processes are not widely used in Al industry, and are economical only for producing high-value ultrapure metals, e.g. solar grade silicon, germanium, etc.

Three-layers electrolytic method

High purity Al can be produced in an electrolytic cell having three liquid layers – two molten Al layers separated by a salt or electrolyte layer. The operating cost of the three-layer cell is comparable to the Hall-Heroult process, however, rather than producing Al from Al_2O_3 , Al is sourced from an impure Al or Al-alloys. The schematic of a three-layer electrolytic cell is presented in **Figure 4**. The bottom layer in the cell (that forms the anode) consists of the impure Al, which sometime is alloyed with copper to increase its density. Al from this layer is electrolytically transferred through the intermediate salt layer to the top higher-purity molten Al layer or the cathode [27-28]. The salt layer is

usually a mixture of fluorides, or fluoride and chloride. Al produced by the three-layer electrolysis has very low impurity concentrations, for example it can achieve non-reactive (such as Ni, Fe) impurities concentration of less than 10 ppm. The three-layer cell is effective in reducing Mn, Cr, Ti, V, Zr, and Ga contents. Such a cell can also lower the concentration of Si, Fe, Ni and Cu [27-28]. There are three patented processes based on this method, namely Hoopes process (USA) [29-30], Gadeau process (France) [31], and S.A.I.A (Societe Anonyme pour l'Industrie de l'Al) process (Swiss) [32]. These three processes are the same in principle, with main differences on the type of electrolyte used, the composition of the anode used, and the temperature of operation.

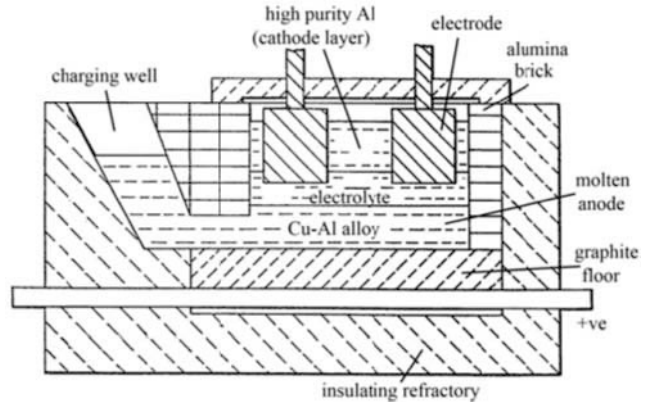


Figure 4 Schematic of three layer electrolysis after Dawless and Jacobs [27]

Zone refining method

The second method to obtain ultrapure Al is through zone refining [33-35]. The process was developed by Pfann [36-37] and its potential for ultrapurification was first recognised when it was applied to produce ultra pure germanium. **Figure 5** shows the schematic of a zone refining process. In this process a small section of a bar is melted using a heater (e.g. using local induction heating). As the bar move slowly along the direction of its length, the molten zone is also move slowly from one end of the bar to the other. The interface between the liquid and solid is maintained planar by solidifying at a slow growth rate with a steep temperature gradient [38]. As impurities are usually more soluble in the liquid they are carried forward with the molten zone so that the re-solidified material is purified at the end where the zone starts its traverse [39].

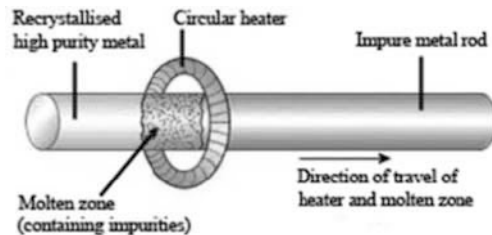


Figure 5 Schematic of zone refining method, modified after [41]

Zone refining is very effective in reducing the amount of strongly partitioning eutectic elements such as Cu, Fe, Si, and Mg in Al. The effectiveness seems to be much lower for Na and Ca and, as with Cr and Mn, the contents of these impurities in Al seem to be the same after twenty zone passes as before zone refining [34].

Kino *et al.* [35] studied the purification of Al by zone refining and concluded that the purification saturated at a particular level and further zone passing contaminated the sample. The optimum conditions found in their study for purification were: zone speed of 24 to 55 mm/hr, zone length less than 30 mm and about 10 times of zone passing. Hashimoto *et al.* [40] produced ultrapure Al, 99.99999%; achieved by repeat zone-passing and cropping, 30 to 60 times.

Fractional solidification method

Another method used for the purification of Al is referred to as fractional crystallization [42-43]. Refining fractional crystallization is based on the fact that when a melt containing one or more solutes is cooled, crystals that solidify have different impurity content than the liquid [38]. The fractional crystallization technique (combined with three layer process) was commercially practiced at Alcoa to produce extremely pure Al (99.99+ %) [27, 44] and the schematic of this technique is presented in **Figure 6**. Purification is accomplished by allowing crystallization to initiate at the top surface of molten metal bath and settle to the bottom of the melt bath. This is carried out by controlling the removal of heat at the surface of the molten liquid. The solid crystals (having higher purity) are packed into the bottom of the apparatus and less pure molten Al is withdrawn through an upper exit port to inhibit contamination of the solid, pure Al adjacent to the bottom of the apparatus [45]. Through this process the purity can be upgraded to 99.993% from a starting purity of 99.91% and the eutectic impurities in the final fraction are lowered from 0.083 wt% to 0.006 wt%. However, this process does not remove Ti, Zr, V, Mn, and Cr.

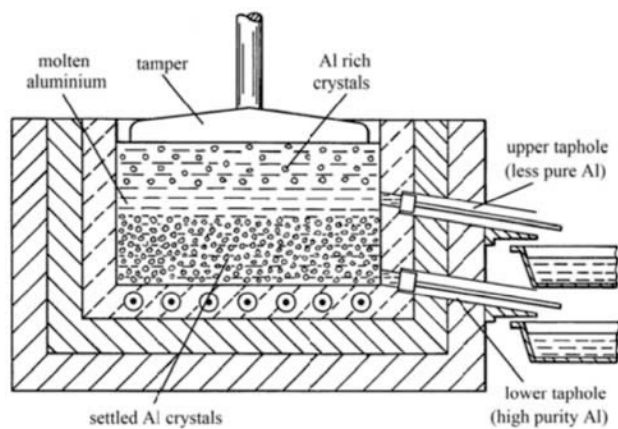


Figure 6 Alcoa fractional crystallization process for purification of Al modified after [27]

Recent Activities in Al Refining

There have been a number of recent studies in the removal of non-reactive metal impurities, such as Ni and Fe, from Al melt. Rhamdhani *et al.* [46] carried out an exploratory study to assess possible methods to remove Ni from Al melt which consist of systematic thermodynamic analysis of various Al-Ni-X systems and experimental studies. Their evaluation on the Gibbs free energy formation of various nickel compounds suggested two potential additives that may be used for removing Ni from the Al melt; i.e. B and P addition for the formation of Ni-borides and Ni-phosphides. They also pointed out the possibility of the formation

of Al-Ni-Zr and Al-Ni-Mg-Zr intermetallics in the Al melt, as nickel can form these intermetallics in Mg melt [47].

They carried out experimental trials on Al-Ni-P, Al-Ni-B, Al-Ni-Zr, and Al-Ni-Mg-Zr to test the thermodynamic analysis results. In all the trials carried out, Ni appeared to remain in the liquid until the later stages of solidification. They reported that upon cooling Ni has invariably precipitated as an Al-Ni intermetallic eutectic phase (divorced or coupled) combined with any available Fe. In the presence of B, the favoured phase was reported to be AlB₂ despite Ni₃B having a lower free energy than AlB₂. Data from plant and laboratory measurements indicates Ni concentration is not affected by Al boride addition.

In the presence of Zr, upon cooling, the elements appeared to form separate Al-Zr and Al-Ni intermetallics. In the presence of P, a formation of metastable Ni₃P particles which re-dissolved in Al melt in an extended period of heating time was reported.

Le Brun and Simensen [48] investigated removal of iron from magnesium rich (>12%Mg) Al melts by precipitation of intermetallics and subsequently separating the magnesium from the Al; perhaps by distillation, fluxing or other treatments leaving a low iron grade of Al. There may be some potential for Ni removal since Ni tends to follow iron in intermetallics in Al.

Techniques in Other Metal Systems

There are a number of other techniques applied in other metal systems for removal of impurities, refining, separation and extraction particular metal. We examine these for potential application to new processes and techniques in Al cast house.

Fire refining of Cu

The term fire refining is commonly used in the processing copper that is in the conversion of matte into blister by removing impurities (S, P, Pb etc). The process is essentially composed of copper oxidation, removal of impurities in the form of their oxides and then reduction of copper oxides to copper. The reduction of copper oxides is carried out by some suitable reductant which could be gas, methane or coal [49-51]. The low free energy formation of Al₂O₃ precludes the use of this approach in Al melt.

Refining of Pb (Removal of Cu, Bi, Ag, and Au)

The common process to remove Cu from Pb is through a double stage process, i.e. segregation and precipitation [52]. In segregation process, the temperature of lead bullion is reduced to lower the solubility of Cu. The Cu separates from the melt and moves to the surface due to its lower density. The Cu mixes with other intermetallics on the surface forming a dross. Following removal of this dross, the lead melt is reheated and sulphur (e.g. in the form of pyrite or sodium sulphide) is then added. This will form insoluble copper sulphides which can be separated.

Bi is removed from Pb by the addition of Ca and Mg which form stable intermetallics (Ca₃Bi₂ and Mg₃Bi₂). These intermetallics (which have higher melting point than Pb, ~ 420°C) are insoluble and form crust/dross on the top of the molten lead. Bismuth content could be reduced from 0.05% to 0.001% through Betterton-Kroll process [53]. Mg-Ca as well Ca-Al alloys have been used to remove Bi from Pb [54-55].

Similarly, Ag and Au can also be removed by addition of Zn. Ag is removed in the form of Ag-Zn alloy which floats on the top of molten Pb. The Ag-Zn alloy are skimmed from top and processed for the recovery of Ag [56].

Al boride treatment is a similar process, i.e. addition of a reactant to produce a product which sinks or floats. However, there seems to be no equivalent for removal of nickel.

Refining of metallurgical grade (MG) Si

The rapid growth in the demand of solar photovoltaic (PV) cell results in the shortage of solar-grade (SOG) silicon feedstock. Metallurgical grade (MG) silicon (98-99% Si) has been shown to be a good alternative Si source. There are a number of techniques that can be used to remove impurities (particularly B and P) to obtain ultrapure Si from MG Si. The most common is through the use of directional solidification [57] which is similar to the concept of zone refining. Three layer electrorefining process [58] and a combination of electron beam and plasma melting with directional solidification [59] have also been used to remove B and P from MG Si. There also a number of works on removing B and P impurities by slag absorption [60]. It has been suggested by Islam *et al.* [61] that the B and P partition ratio to the slag can be improved by applying electrical potential across the slag-metal interface.

Distillation and separation of high vapour pressure metals

A fractional distillation process can be used to refine or separate metals which have considerably different vapour pressure compared to other metals in the mixture. An example is in the refining of Zn from a mixture of Cd, Zn, Pb and Fe. This is carried out in an externally heated double distillation column. In the first column the metal mixture is charged from the middle and during the travel down, the higher vapour pressure metals such as Zn and Cd are evaporated while the rest remain in the downflow. The Zn and Cd vapours travel to the second column where Zn tends to condense in the downflow and Cd vapour leaves at the top. The same approach can potentially be used in Al melt, for example, for separating Mg from Al melt. However, the low vapour pressure and high melting point of Ni, preclude this approach for removal of Ni from Al.

Concluding Remarks

Current refining methods in cast house are targeted specifically at inclusions, Na and H₂ and have little scope for controlling Ni or V. Boride treatment can be used for vanadium removal but when applied to common alloys will add considerable expense. There are still scopes for improvement of control of V by boride treatment, particularly in optimizing the process and maximizing the economic. Looking further afield at methods for producing super purity metal; they can remove Ni and V but are too expensive for everyday alloys (they would roughly double the cost). Neither does examination of refining methods in other non-ferrous metals produce any promising lines of enquiry.

Despite investigation into potential Ni removal systems, no suitable system has been identified at present. It is not definitively known what form the Ni take in primary smelter metal. In the discussion above we assume they are dissolved in the liquid Al. If however, there were particles containing Ni and V present, they could be filtered out. This possibility needs to be investigated.

Grandfield *et al.* [2, 62] suggested various approaches to managing the issue of increasing Ni and V along the value chain as shown in Figure 7. Interventions to remove or control impurities can be applied at any stage starting from the processing of pet coke and alumina refining.

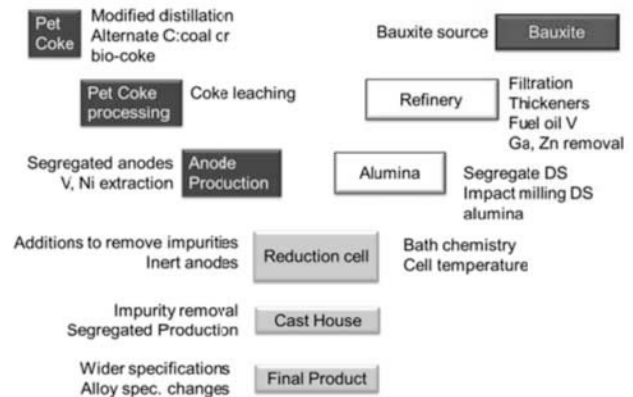


Figure 7 Al value chain and possible interventions to manage impurities at each stage

In conclusion, cast houses cannot at this stage provide easy solutions to the issue of increasing Ni and V concentrations. While AIB treatment may be improved to reduce costs of V removal the economics remains questionable for many products and there appears no means of removing Ni. Strategies throughout the whole process chain will need to be considered. These may include:

- Widening alloy specifications (if possible)
- Segregating process streams
- Blending
- Removing impurities from dry scrubber (DS) alumina.

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