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AIR POLLUTION CONTROL
IN THE
PRIMARY ALUMINUM INDUSTRY

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4.0 Sources and Characteristics of Effluent Releases

The airborne effluents from primary aluminum reduction plant operations include dusts of carbon and alumina from materials handling and preparation, and particulates and gases evolved from potlines, anode bake furnaces and cast houses. The greater quantity (and potentially most damaging) are evolved in the actual electrolytic reduction process at the potline. An understanding of the operations causing the release of the various kinds of pollutants, and the identification of sources, provides a basis for consideration of abatement by control over process variables and for the selection of effective pollutant removal equipment. The following paragraphs discuss factors which influence the production of effluents.

4.1 Potline Effluents

The quantities and composition of potline effluents vary within wide limits among modern aluminum smelters, being strongly influenced by operation conditions such as temperature, bath ratio, frequency of anode effects, and method of crust breaking. Moreover, the effluent may vary with time for any given plant, due to gradual changes which may occur in potline operations.

Normal cell operation is interrupted by occasional anode effects, cell working to introduce alumina feed, periodic tapping of molten aluminum and in the case of prebake cells, the periodic changing of anodes.

According to one investigator, the normal fluoride evolution from a crusted-over cell is approximately 15 pounds F per thousand pounds of aluminum produced but during an anode effect the fluoride evolution increases to approximately 378 pounds per thousand pounds of aluminum, 4.1/. Normally individual cells in this country may experience from less than one-half to two anode effects per cell day. The duration of an anode effect is dependent upon how quickly the cell operator corrects it and may range from five to fifteen minutes.

Breaking the crust of the cell for a cell working causes the fluorine evolution to rise to approximately 53 pounds per thousand pounds of aluminum. 4.1/ The duration of a cell working varies according to the size and type of the cell and whether or not the cell is equipped with automatic crust breakers. With the automatic crust breaker on a prebake cell, working is accomplished very quickly, taking only one or two minutes. For a normal size prebake cell of approximately 90,000 amperes, a manual working may be accomplished in five to ten minutes depending upon the hardness of the crust. Soderberg cells and side-working prebake cells are normally worked by means of a pneumatic crust breaker similar to a paving breaker. A working may be accomplished in approximately five minutes on a 90,000 ampere side-worked cell.

Tapping and changing anodes cause the least increase in fluorine evolution depending upon how much of the molten electrolyte is exposed.

Sulfur oxide effluents originate from the coke and pitch from which the sacrificial anodes are made.

4.1.1 Composition of Potline Effluents

A typical prebake cell effluent, derived from published information in the literature, and the Industry Questionnaire, is shown in Table 4.1. These data indicate that:

a) Roughly 25-63 pounds of particulates are released per 1000 pounds of aluminum produced, of which 10-25 percent of the weight is fluorine content.

b) Gaseous fluorine content is approximately half again the weight of fluorine contained in the particulates.

Table 4.1

Reduction Cell Effluents

Component	Quantity lb/M lb Al	
	European 1/	U.S. 3/
CO_2	1500	-
CO	250	-
SO_2	6.5	30 2/
"F" (Gas)	10.3	13.1 3/
"F" (Solid)	6.3	8.8 3/
Total "F"	16.6	22.5 3/
Total Solids	25 to 63	45.6 3/

1/ Ref. 4.2/, 4.3/, 4.4/, 4.5/, 4.6/, 4.7/, 4.8/, 4.9/

2/ Estimate based on 3 percent sulfur in anode coke.

3/ Industry Questionnaire, Weighted Average Response.

J. L. Henry, contributor to a 1962 international symposium on the extractive metallurgy of aluminum 4.2/, reviewed the nature of reduction plant fumes. The following summary of effluent compositions is based largely on this review.

Particulate Composition and Particle Size

The particulate phase of the cell effluents contains material derived from dusting of the alumina and other raw materials during the feeding operation of the cells, solid matter which originates from the volatilization of the fused salt bath, and material mechanically entrained by the air sweep over the cell surface into the collection system. The greatest portion of the airborne particulates consists of alumina from dusting; some of the alumina is formed by thermal hydrolysis of the volatized bath materials. Carbon particles result from the mechanical and electrochemical dusting of the anodes.

Other components have been identified in the particulate matter including cryolite (Na_3AlF_6), aluminum fluoride (AlF_3), calcium fluoride (CaF_2), chiolite (Na_5Al_3Fl4) and iron oxide (Fe_2O_3).

Particle size distribution is a principal determining factor in the particulate removal efficiency for most types of air pollution control equipment, and knowledge of the size distribution for a given pollutant may aid in estimating the removal efficiencies of alternative selections among types of removal equipment. If the fractional removal efficiency characteristic of a piece of control equipment is known and if the particle size distribution of a pollutant can be determined by the same or comparable measuring equipment used for determining the fractional efficiency, then these data may be combined to calculate an overall removal efficiency for the equipment operating on the pollutant dust in question.

Published or reported cell effluent particle size distribution data are sparse and techniques for measurement are subject to variations, even among different investigators using similar equipment, so caution should be exercised in drawing conclusions from these data or in comparing data from one source with those from another.

However, a limited amount of available information provides a basis for estimating the performance of some types of control equipment applied to potline effluents.

Reported determinations of particle size distributions of the dust and fume collected in primary effluents are plotted in Figure 4.1. Two plots are shown for prebake potlines, one reported as the average of four samples of pot emissions, the other as the average of five samples of electrostatic precipitator intake. A single plot of average samples is shown for HSS Soderberg. No comparable data have been obtained for VSS Soderberg effluents.

These plots are illustrative of the comparative size characteristics of the primary dusts from two types of cells. The slopes of these data give an indication of the range of particle sizes in the samples and the placement of the curves on the plot indicates that a substantial fraction of the prebake and HSS particulate weight is submicron, or in the range where particulate removal efficiencies of most equipment are low.

Additional particle size data are reported in Appendix 4A.

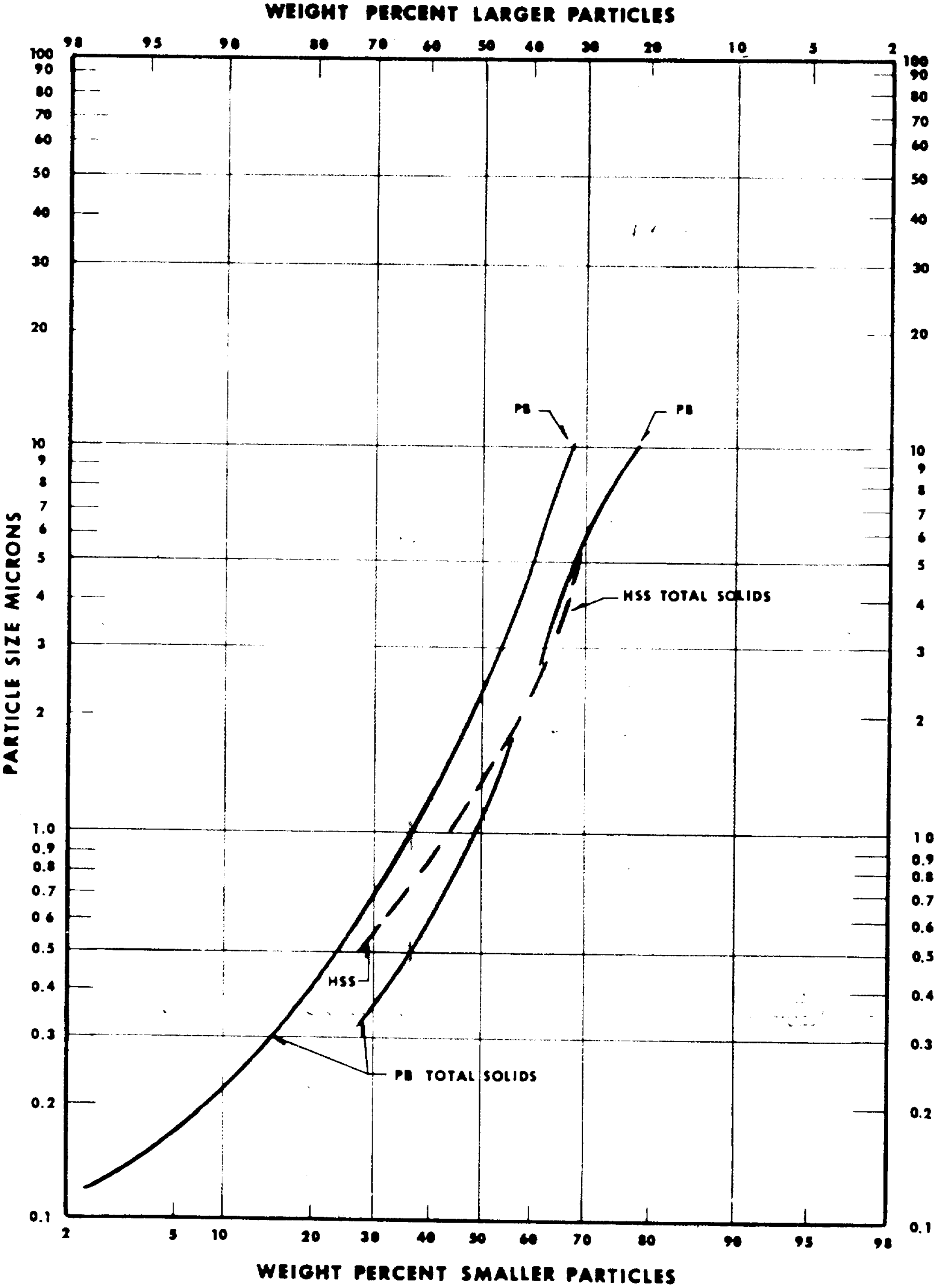
Gaseous Composition

The gaseous phase of the cell effluent, before coming into contact with air, consists principally of carbon dioxide and carbon monoxide formed by the oxidation of carbon anodes by oxygen released from Al_2O_3 on electrolysis. Although the mechanism of formation is subject to argument, the variation in volume ratio of the two gases during the normal cycle of cell operation is generally known. The ratio of CO_2 to CO decreases when the cell temperature is abnormally high and also during the periods when the anodes are polarized (anode effect). The carbon dioxide content of the unburned gases varies between 60 and 85 percent; the balance is largely carbon monoxide. Contact of the hot gases with air results in a substantial decrease in the carbon monoxide through combustion.

Other gases may be found in small amounts during cell operation. These include sulfur dioxide (SO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon

FIGURE 4.1

PARTICLE SIZE WEIGHT DISTRIBUTION
POTLINE PRIMARY EFFLUENT



INDUSTRY REPORTED DATA

disulfide (CS_2), silicon tetrafluoride (SiF_4); hydrogen fluoride (HF), and water vapor.

During the period of an anode effect, fluorocarbons are known to be produced. These consist almost entirely of carbon tetrafluoride (CF_4) together with very small amounts of hexafluoroethane (C_2F_6).

Fluorine

Henry reports that the ratio of gaseous to particulate fluoride in reduction cell fumes varies over a range of about 0.5 to 1.3. These values are given for fumes which have burned in contact with air. Weighted average data from the Industry Questionnaire indicate that this ratio is about 1.2 to 1.7 for prebake and HSS Soderberg cells and about 3.0 for VSS Soderberg cells with hydrocarbon combustors. Unburned fumes usually show a lower ratio of about 0.3, according to Henry. Burning of the hot gas-particulate mixture when it contacts air results in thermal hydrolysis of some of the particulate fluoride with the formation of additional hydrogen fluoride.

Thermal hydrolysis of volatized bath materials appears to be responsible for a substantial part of the hydrogen fluoride found in reduction cell fumes. This reaction of solid or vaporized fluorides with water vapor at elevated temperatures takes place primarily at the point where the hot gases escape through vents in the crust.

A source of hydrogen is necessary for the generation of hydrogen fluoride. Water vapor in the air is a contributor of part of this hydrogen. Other sources include residual moisture in alumina and bath raw materials and hydrocarbons in the carbon anodes.

Some gaseous hydrogen fluoride is removed from the effluent stream by interaction with the contained particulate matter. Chemical reaction is responsible for some of this pickup, while some is due to chemisorption, absorption, and adsorption.

While the determination of total fluoride content of fumes may be quite reliable, estimates of the distribution of fluoride between gaseous and particulates forms is subject to uncertainty [illegible] factors [illegible] the degree of thermal hydrolysis [illegible] of the gas and method of separation of gas and particulates during sampling.

Sulfur Oxides

The sacrificial carbon anodes of aluminum reduction cells are made from calcined petroleum coke which characteristically contains sulfur. Whereas coke with a maximum sulfur content of 2.5 percent was once readily available, it has become scarce and smelters now buy coke with as much as 5 percent sulfur. The average petroleum coke now in use may contain 3 percent.

Since this coke has already been calcined at temperatures above the anode baking temperature, the sulfur is fixed and will be released only as the anode is consumed in the electrolysis process. Depending on sulfur content of anode carbon, the SO_2 effluent may range from 15 to 50 pounds per 1000 pounds of aluminum produced.

Soderberg Effluents

The effluents from Soderberg cells have, in addition to the constituents mentioned above, the characteristic of containing the hydrocarbons evolved by the baking of the anode paste in the cells. The presence of these hydrocarbons, which are in gaseous form at the cell operating temperatures, complicates in some degree the emission control problems associated with Soderberg cells. If they cannot be converted by combustion to stable gaseous compounds the hydrocarbons will condense to tarry compounds which are difficult to handle and remove from the gas stream. As will be noted in a later section, the collection and combustion of these materials is practical with the VSS Soderberg cell, but not with the HSS Soderberg cell. In the latter case the problem of tar separation becomes somewhat similar to that encountered in prebaked anode furnace plants, where similar tars are present in the effluents.

4.1.2 Factors Influencing [illegible] Fluorine Effluent Generation

J. L. Henry reported 4.2 on experimental work which established correlations between three cell operating parameters and effluent production for a 10,000 ampere laboratory experimental prebake type aluminum reduction cell. It was shown that increasing bath ratio (NaF/AlF_3), increasing alumina content of the bath, and decreasing temperature all tend to result in a decrease in the fluoride content of cell effluent. Table 4.2 summarizes the findings of these tests.

Table 4.2

Experimental Effect of Three Operating Variables on Fluoride Effluent

Range of Variables			
Bath Ratio	Alumina Content	Temperature	Fluoride Effluent
(1.44 to 1.54)	4%	975°C	31% Decrease[1/]
1.50	(3% to 5%)	975°C	20% Decrease[1/]
1.50	4%	(982 to 972°C)	24% Decrease[1/]

[1/] Within range of variable denoted by ( ).

Henry calls attention in his paper to the fact that "determination of the effect of operating variables on the fluoride emission from electrolytic reduction cells is difficult to accomplish with a high degree of certainty. This is true even with small-scale experimental cells operated by research personnel. It appears from the work reported here, however, that cell temperature, bath ratio, and alumina concentration are the most important variables affecting total fluoride emission".

The absolute relationships reported by Henry may not hold for full-scale cell operation.

4.2 Carbon Plant Effluents

Aluminum reduction cell anodes and cathodes are made from anthracite and/or petroleum coke, bonded by pitch and baked to form solid carbon masses. The preparation of the carbon materials, consisting of crushing, grinding, classifying, blending of carefully sized fractions, and mixing with pitch binder, is carried out in the green mill. In all but a few cases, this carbon plant operation is carried out on the reduction plant site, the exceptions being plants utilizing prebaked anodes and cathode blocks which are shipped to the plant already fabricated.

The effluents from these operations consist of coke and coal dusts and fines generated by comminution, screening, and materials handling. Control is practiced to maintain plant housekeeping and industrial hygiene standards. Effluents are generally coarse particulates, easily controlled by collection to bag houses, and do not constitute a significant air pollution problem beyond the boundaries of an aluminum reduction facility.

Volatile hydrocarbon fumes are generated to a limited extent by the paste mixing operation in which the hot pitch binder is added to the dry materials. This effluent is usually vented directly to atmosphere. In some operations, however, these fumes are partially removed from their gas streams by using a wet scrubber.

4.3 Bake Plant - Effluents

For plants using prebaked anodes the carbon paste is pressed to green forms and baked for extended periods, during which time effluents are generated and released.

Bake plant effluents may include products of firing combustion, burned and unburned hydrocarbons derived from the heating and carbonizing of the paste binder pitch, SO_2 and SO_3 derived from the carbon paste materials, and fluorine. The source of the latter is recycled anode butt scraps which carry absorbed or adherent bath materials back into the anode cycle.

Little information has been gathered or published concerning the quantitative amounts of coke plant effluents. A very limited amount of testing has been carried out on baking emissions. The order of magnitude of the problem is indicated in Table 4.3, supplied as an average by a multi-plant aluminum producer. It is reported that total F effluents can be maintained at less than 0.4 pound per ton of aluminum produced by exercising particular attention to cleaning the spent anode butts of adherent bath before they are crushed for recycle.

Table 4.3

Anode Baking Ring Furnace Emissions [1]

Flow Rate, cfm	75,000 - 184,000
Stream Loading, gr/cf	
Total Solids	0.021 - 0.10
HF	0.003 - 0.03
Pitch Condensate	0.01 - 0.30
Quantities, lb/1000 lb Al	
Total Solids	1.0 - 5.0
Hydrocarbon	0.25 - 0.75
Total F	0.15 - 0.75
Sulfur	0.35 - 1.0

[1] While the direct fired ring furnace has been the normally used type for prebaked anodes, attention has been given to the development of continuous tunnel kilns for this purpose. Combustion conditions are significantly different and zonal temperature control closer, with one result being that the above emission levels may be reduced by factors of 0.01 in total solids and 0.02 in hydrocarbons, fluorine, and sulfur.

4.4 Cast House Effluents

Cast house operations include the receipt of molten metal in tapping crucibles from the potlines, transfer to holding furnaces or casting in large sows for later remelt, fluxing for the removal of impurities, alloying, and casting into ingots or billets. Effluent releases from these operations consist largely of fluxing fumes, periodically evolved.

Furnaces are usually gas-fired, and in themselves present no potential pollution problem.

Blended metal from the holding furnaces can be gas-fluxed or salt-fluxed for the removal of certain impurities such as oxides, bath electrolyte, or gas inclusions and the skimmings, or dross, subsequently treated for metal recovery.

Gas fluxing involves the bubbling of chlorine, nitrogen, argon, helium, or mixtures of chlorine with any of the inert gases, through the molten metal in the holding furnace. Salt fluxing, in which the salt is added to the bath surface, may utilize hexachlorethane, aluminum chloride, and magnesium chloride. In all cases where chlorine or chlorine compounds are used for fluxing, copious quantities of fumes are evolved, which must be collected and removed from the working area and may or may not be treated. The fume is primarily aluminum chloride which, in the presence of atmospheric moisture, may hydrolyze to HCl and Al_2O_3. If a melt is overfluxed, free chlorine may evolve. Traces of fluorine may be present in the fumes, originating with electrolyte impurities fluxed from the metal.

4.5 Other Effluents

The handling of dry bulk materials, alumina, cryolite, and fluorspar is accompanied by dusting at transfer points. These particulate effluents are normally an industrial hygiene problem but may create an air pollution problem. Normally they are collected at the points of evolution and returned to the handling systems.

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