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THE CHARACTERISATION OF ALUMINIUM REDUCTION CELL FUME

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Abstract

The nature of the fume emitted by aluminium reduction cells with pre-baked anodes has been investigated. The gaseous and particulate contributions under different conditions of cell operation have been assessed and the constitution and particle size distribution of the dust determined by chemical and X-ray examination, together with optical and scanning electron microscopy.

Approximately 50% of the fluorine emission is in the form of hydrogen fluoride. The particulate material exhibits a double size distribution with one fraction consisting substantially of dust greater than 5 μm diameter and the other of fine material considerably less than 1 μm diameter. The principal components of the coarse fraction are alumina, carbon and frozen droplets of cryolite, whilst the fine fraction appears to consist mainly of condensed fluoride vapour approximating in composition to chiolite ($5NaF.3AlF_3$). This fine particulate material accounts for about 35% of the total fluorine emission from the cells.

Some parallel observations on the character of the fume evolved from vertical stub Soderberg cells are also discussed. The principal differences are that approximately 90% of the fluorine is present as HF, and that the dust, and particularly the alumina content, is lower than from a prebake cell.

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1. Introduction

With the increasing concern over environmental pollution and the more stringent standards being applied to smelter emission it is important to have a detailed knowledge of the nature of the fume evolved from aluminium reduction cells. This will allow a more informed approach to the design of fume treatment plant, and enable a more accurate assessment to be given of the effect of the fume on the environment. A fundamental investigation was therefore made of the characteristics of the emission from prebake anode cells and from V.S. Soderberg cells. The techniques used included particle size separation by cyclones, separation of gaseous and particulate fluorides using molecular filters, and analysis of the collected dusts chemically, by X-ray crystallography and by optical and electron microscopy.

2. Experimental

The prebake anode cells examined were hooded, and fume for analysis was drawn from the off-take duct close to the cell. Soderberg fume was sampled immediately before a fume treatment plant, having passed through individual cell burners and a moderate length of ducting. Some losses of coarse particles thus occurred although these would include only a small proportion of the total fluorine; the fine particulate and HF were largely unaffected. Fume was drawn isokinetically at a rate of 20 m^3/h through an apparatus* comprising identical twin four-inch cyclones in series followed by a 293 mm diameter molecular filter. Sufficient dust was collected in the cyclones and on the filter for weighing and for chemical analysis of the main constituents, and the dust-free gas could then be sub-sampled by drawing it through bubblers or alkali-impregnated filters in order to measure the HF content. The use of a mixed cellulose ester molecular filter, having a very low ash content, allowed direct analysis of the filter plus dust. Alternatively the filter could be dissolved away in acetone and leave the dust or, if sufficient was present, solid could readily be removed from the smooth surface of the filter.

The cyclones were designed and calibrated each to collect approximately 50% of spherical particles of unit density having a log-normal size distribution and a mean diameter of 4 μm. The separating efficiency was deliberately reduced by decreasing the angle between the intake tube and the cyclone axis to 30°. By measuring the collection efficiency of an unknown dust in the 1st and 2nd cyclones, i.e. the quantities collected in the two cyclones and on the filter, calibration curves enabled the mean effective diameter and the spread about the mean to be calculated if the distribution was log-normal. The apparatus has the advantage of measuring

* Supplied by A.B. Svenska Fläktfabriken, Stockholm. See S.F. Review 1/1954 for further details.

the effective size of the particles in air, regardless of shape or density; this is the important parameter in considering their behaviour in the atmosphere or in a treatment plant.

Several methods were used to collect fine particles in a form suitable for microscopic examination. In the cascade impactor cell off-gases were passed through four progressively narrower slits, and successively finer particles were impacted onto slides placed closely after each slit. Size separation was fair, but some coagulation occurred on the slides and the method was unable to trap particles below 0.3 μm. The thermal precipitator used a hot wire to impact particles onto glass slides or carbon-coated grids placed close to the wire. Particles below 5 μm diameter are quantitatively trapped and Fig. 1 shows an electron micrograph of prebake cell fume collected in this way. A better sampling method, however, was to draw fume through a fine pore (0.03 μm) molecular filter and to examine the dust trapped at the surface by means of the Stereoscan electron microscope (Fig. 2 prebake fume, Fig. 4 Soderberg fume).

The coarse particulate collected in the cyclones was examined directly with an optical microscope (Fig. 3).

For air within the factory or in the surroundings, a simple separation of fluoride into particulates and HF was made by drawing gas through two molecular filters placed in a single holder, the upper one being clean and the lower impregnated with sodium formate solution. Particles were trapped with 100% efficiency at the surface of the upper filter even if much smaller than the pore size (the largest available, 8 μm, was used to reduce pressures and increase the flow rate). The lower filter absorbed 250-300 μg of HF with high efficiency but for larger amounts, obtained for example when sampling from a duct, a second impregnated filter was used, or the gas was passed through a clean filter followed by a simple bubbler train. It was shown that a small quantity of HF was absorbed on a dust-covered clean filter, but the amount was only a small proportion of the total except at very low HF concentrations (below ~2 $\mu g/m^3$). For higher concentrations the filters gave an effective separation of solid and gaseous fluorine.

3. Results

3.1. Prebake cell fume

Dust was collected in the cyclone apparatus predominantly in the first cyclone or on the filter, the quantity in the second cyclone being only 1 - 2% of the total. From this distribution the characteristics of the cyclone indicate the dust to be mainly in two size ranges, below 2 μm effective diameter or over 6 μm. (The collection efficiencies for 2 μm and 6 μm particles are approximately 2% and 98% respectively). Fig. 2 shows a Stereoscan micrograph of fume collected after passing through the cyclones, i.e. with coarse dust removed. The mean particle size is about 0.2 μm and all are below 1 μm in diameter. Fig. 1 is an electron micrograph of total fume collected with the thermal precipitator. A large number of sub-micron particles are evident but there are many of 1 - 2 μm diameter and a few over 2 μm. Fig. 3 is an optical micrograph of dust collected in the cyclones during a period of quiet cell operation. Predominantly this is a coarse dust - sieving gave approximately equal weights of + 20 and - 20 μm fractions - although a few particles as small as 2 - 3 μm are present.

X-ray analysis showed the fine dust to consist principally of chiolite, $5NaF.3AlF_3$, possibly with traces of cryolite, $3NaF.AlF_3$, and $NaF.AlF_3$. No alumina was detected. Chemical analysis gave a fluorine content of about 50%, the difference from chiolite (58% F) probably being due to partial hydrolysis.

The coarse fraction consists of transparent spheres of low refractive index, probably of splashed cryolite, and of irregular light and dark particles probably of alumina and carbon. X-ray analysis indicated the predominant species to be α-alumina and cryolite. Carbon from the anodes was ~20% of the dust but is not easily detected by X-ray crystallography. The fluorine content was much lower, at ~20%, than in the fine dust, due mainly to the presence of the alumina and carbon.

Numerous measurements were made during different periods of cell operation and an estimate of the fluoride evolved during a normal day was thus obtained, Table I. The proportions are approximately,

coarse particulate	20% of total fluorine
fine particulate	35% of total fluorine
HF	45% of total fluorine.

Table I Estimate of daily fluorine evolution from a 100 kA prebake anode cell.

Kilograms per cell-day

	Total dust		Fluorine			
	Coarse	Fine	Coarse	Fine	HF	Total
11 periods of quiet cell operation (crusted over), each of 90 min.	2.51	3.26	0.68	1.18	1.86	3.72
1 period of quiet cell operation with some exposed bath, 80 min.	0.51	0.78	0.17	0.27	0.30	0.74
12 periods of 30 min. each including break and feed	4.16	5.83	0.95	2.04	2.54	5.53
1 period of 8 min. including a light with poling of 2 - 3 min.	0.98	0.82	0.19	0.22	0.04	0.45
Total for day, kg	8.16	10.69	1.99	3.71	4.74	10.44
Equivalent, lb	18.0	23.6	4.4	8.2	10.5	23.1
Percentage of total fluorine			19.1	35.5	45.4	
(In round figures			20	35	45	)

3.2. Soderberg fume

As previously noted, the Soderberg fume was sampled at the entry to a fume treatment plant and thus represented the evolution from a large number of (100 kA) cells. The effects of breaking, feeding and other cell operations were therefore averaged out. The numerous sampling runs which were carried out using the cyclone apparatus all gave similar results with respect to dust load, coarse and fine particulate fluorine and HF evolution.

The principal difference from the prebake cell was that a high proportion (approximately 90%) of the fluorine was in the form of HF. Again very little dust was collected in the second cyclone and 97 - 98% of the dust was trapped either in the first cyclone or at the final filter; hence it could be concluded that the particulate was predominantly either over 6 μm or below 2 μm in effective diameter. Approximately 75% of the dust was in the fine fraction, but there was some deposition of coarser particles in the ducting so that the proportion of fines nearer the cells was probably rather less than this.

Chemical analysis showed fluorine contents of about 15% and 18% in the coarse and fine fractions respectively. The average distribution of fluorine was

Coarse particulate	1.5% of total fluorine
fine particulate	7.5% of total fluorine
HF	91.0% of total fluorine

Fig. 4 shows a Stereoscan micrograph of the fume. It contains predominantly sub-micron particles and is little different in appearance from prebake cell fume. X-ray crystallography indicated the presence of cryolite and chiolite in both coarse and fine dusts but alumina was not detected in either. The moisture, including combined water, was high in both fractions at 12 - 25% and analysis for sodium and aluminium was consistent with a complex mixture probably of chiolite or cryolite and their hydrolysis products. The coarse dust contained about 25% carbon and included both tar and anode flakes, but the fines showed only 3 - 4% carbon.

The proportions of solid and gaseous fluorides were also measured on several occasions at the potroom roof. An average of 88 - 90% of the total fluorine was HF, a value similar to that in the collected gases.

4. Discussion

Clearly the quantity and type of fume emitted from a reduction cell will depend to a considerable extent on the cell design and on the operating techniques used. A sandy alumina, for example, will give more dust than a floury alumina, particularly from a prebake cell, and a cell run cold will give less fume than a hot cell especially if the crust of the hot cell is not well formed. There are, however, general characteristics of prebake and Soderberg fume that can be summarised:

4.1. Prebake cell

(a) There are approximately equal amounts of solid and gaseous fluorides.

(b) A large part of the particulate fluoride is sub-micron in diameter.

(c) The fume has a relatively high alumina content.

4.2. V.S. Soderberg cell

(a) Approximately 90% of the fluorine is present as HF.

(b) The fume has a low dust content (unless cell burners are unlit when tar levels will rise).

(c) There is little or no alumina.

The formation of the different components may be considered briefly. It is believed that initial vapourisation of the bath occurs as $NaAlF_4$, but the solid is unstable and disproportionates, probably to AlF_3 and $5NaF.3AlF_3$ (chiolite). In a prebake anode cell the gases evolved at the anode will carry droplets of flux, together with the evaporated bath material and some anode carbon flakes, through the crust to the atmosphere, where hydrolysis of the AlF_3 (most susceptible) and of some cryolite and chiolite will occur. Alumina from the crust will be carried into the gas stream. In a V.S. Soderberg cell similar evaporation and splashing of the bath will occur, but the opportunity for forming HF is increased by two factors, (a) the presence of hydrocarbons and hydrogen from the anode, either reacting directly or after burning to water and (b) the high temperature at which the fume is in contact with moist air after passing through the burner. It is not known which is the more important factor, but clearly both the fine and coarse particulates react extensively to form HF.

An accurate assessment of particle size distribution is made difficult by the different components present and by the wide range of particle sizes. Equal weights of 0.2 and 20 μm particles of equal density, for example, will have 10^6 times as many of the small as of the large. Thus, photomicrographs, which for clarity must be of low particle density, are statistically unlikely to show the larger particles.

Division into a coarse and a fine fraction is effected by the cyclone apparatus and the relative quantities of each, which vary widely with the cell design and operation, can be measured. The distribution between cyclone 1 and 2 and the filter shows that little material is present with an effective diameter around 4 μm, equivalent approximately to 1 - 2 μm for the materials in the dust (these have a density of about $2 g/cm^3$). Micrographs of the fume and of the collected cyclone dust confirm that most of the particles are either sub-micron or have diameters of 2 - 3 μm or above, and for practical purposes these are the important classifications. Sub-micron particles, for example, behave in some ways very much like gases; they show almost no tendency to deposit from the atmosphere and are difficult to collect in cyclone or spray treatment plants. Particles above 5 μm effective diameter are readily removed by such treatments and are deposited from the atmosphere.

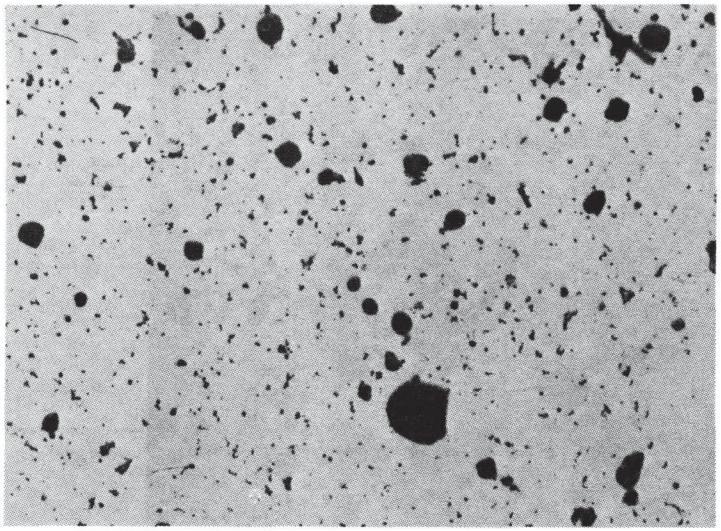

Fig.1 Electron micrograph of prebake cell fume collected by the thermal precipitator(×3,000)

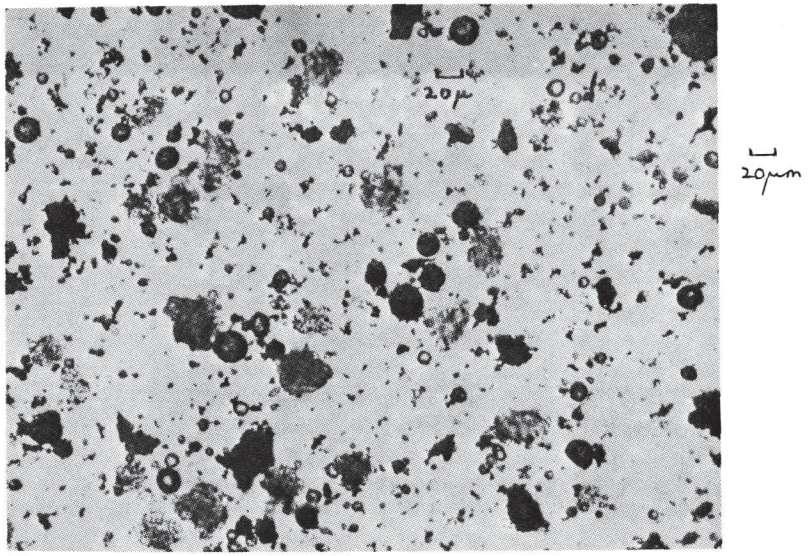

Fig. 3 Optical micrograph of prebake cell fume collected in cyclone 1. (×250)

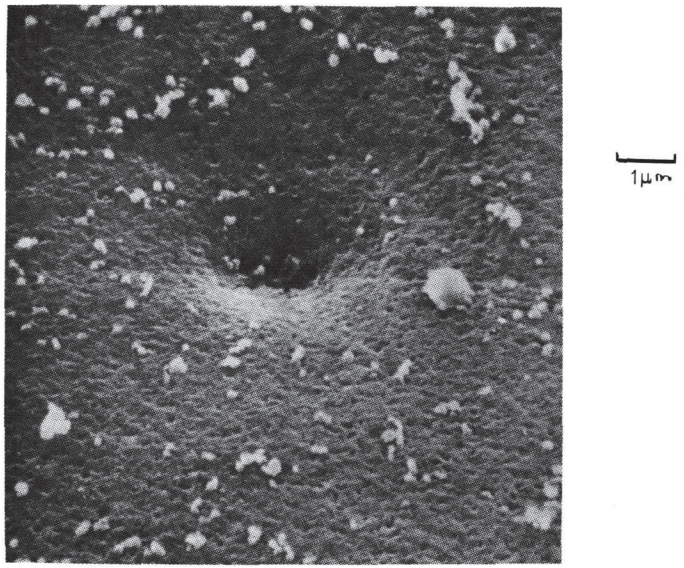

Fig. 2 Stereoscan micrograph of prebake cell fume which has passed the cyclones. Collection was on 0.03 μm pore size Millipore filter.(×10,000)

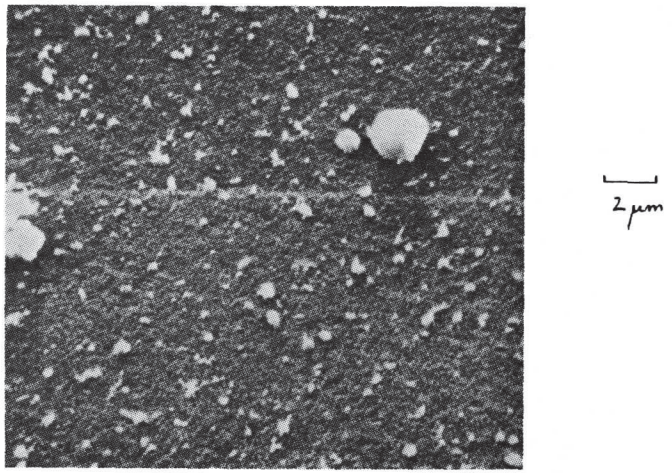

Fig. 4 Stereoscan micrograph of Soderberg fume collected on a Millipore filter (×5,000)