Reduction of Emission of Sulphur Dioxide

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Reduction of emission of sulphur dioxide

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[Plate 3]

The changing pattern of primary fuel consumption will ensure that, by 1975, almost a quarter of the electricity produced in Britain will come from non-fossil fuel sources (Hartley 1964, 1966). Of the remainder, a large proportion will be generated in modern power plant with provision for plume dispersal from stacks between 200 and 260 m tall. These trends represent a considerable advance towards control of the sulphur emission problem, but in most industrialized countries, there is an active interest in the development of processes for removing sulphur compounds before flue gas is discharged and in the possibility of recovering sulphur in a useful form.

Cleaning fuel

There is no immediate prospect of economic removal of sulphur from fuel before combustion in power plant. Residual fuel oil used in Britain has a sulphur content of about 2.5 % and estimates of the cost of catalytic hydrogenation processes for sulphur removal (e.g. de Haas Nieuwchuizen, Akbor, van der Guissen & ter Haar 1966), range upwards from $3.40 per ton; in other terms, sulphur could be recovered from this source at about nine times the market price. Coal received by the Generating Board has a weighted mean sulphur content of 1.7 %, comprising about 0.1 % sulphate, between 0.6 and 1.0 % organic, with the remainder mainly pyrites (H. E. Crossley, private communication, Wandless 1959). It is possible to reduce the pyritic content by physical separation from pulverized coal. Various techniques of separation are under study, e.g. pneumatic, froth flotation, magnetic, bacterial, solvation, but none has yet been shown to be economically practicable (Perry & Field 1967). Consequently, although only 1 to 2 parts/10^3 (by volume) of sulphur dioxide is present in flue gas, removing it is seen as a more promising approach to emission control, despite the engineering problems involved in treating the very large volumetric flow of gas emitted from power plant.

Cleaning flue gas

Many simple chemical reactions are being developed at this time as flue gas cleaning processes. For example, the Claus reaction

$$2H_2S + SO_2 \xrightarrow{Al_2O_3} 3S + 2H_2O$$

is feasible in the laboratory, even at the low levels of concentration appropriate to flue gas (Spence 1964). There are unresolved difficulties in the application of this reaction under power plant conditions, and processes based on catalytic oxidation of sulphur dioxide to the trioxide have so far been developed with more success. For example, the Penelec/Monsanto process, currently operating on pilot scale (Stiles Horlacher, Bachelor & Bartman 1968) recovers a marketable quality of sulphuric acid (78 %) by condensation and precipitation of the acid mist from the flue gas stream. In a second scheme (Kiyoura 1966), ammonia is injected to the gas stream after the catalytic oxidation step, and ammonium sulphate recovered by electrostatic precipitation, or bag filtration. In Eastern countries, ammonium sulphate has a ready market as a fertilizer.

The sorption–desorption of sulphur dioxide on carbon has also been developed on the engineering scale. A temperature restriction applies, however, since sulphur dioxide pickup by carbon falls off rapidly above 100 °C. In the Reinluft process, sulphur dioxide, which is retained on coke as sulphuric acid, is recovered by heating to about 400 °C (Johswich 1962). Carbon is lost as carbon dioxide during decomposition of the sorbed sulphuric acid, and the physical and chemical properties of the sorbent are changed irreversibly (Billinge 1965). Several pilot plants have been installed, mainly in Germany, but difficulties in operation have arisen through the combustibility of the sorbent. This hazard is enhanced by the catalytic action of metallic contamination picked up by the sorbent in service. The problems of thermal regeneration are avoided in the Sulfacid (Lurgi) and the Hitachi versions of this process (Slack 1967). In both, sulphuric acid is leached from the coke bed by water washing techniques; the dilute acid recovered has a limited industrial value.

Salt formation is the basis of several processes. The simplest systems discard the salt formed, and schemes of this type are operating on full plant scale at two London power stations. The Battersea process relies mainly on washing sulphur oxides from flue gas using natural river water, completing the removal with a final wash using river water to which a little chalk has been added (Hewson *et al.* 1933). The Howden–I.C.I. process recycles a wash-water containing sufficient added alkali to react with all of the sulphur oxides removed; a fraction of the circulating water is filtered to collect the waste salt for disposal (Nonhebel 1936). The formation of calcium sulphate can also be achieved by injecting dry limestone into the furnace gas, as in the Combustion Engineering–Detroit Edison process; the sulphate in this case is recovered, together with fly-ash, in wet scrubbers which are packed with moving spheres to avoid plugging. Several regenerative processes have also been developed. The Fulham–Simon Carves process involves reaction of sulphur oxides with ammonia liquor, ammonium sulphate being recovered after autoclave treatment of the spent solution from the absorber towers (Wood 1960). The Board's interest is currently centred on the alkalized alumina process, proposed by the U.S. Bureau of Mines (Bienstock, Field & Myers 1964). The sulphur oxides react with sodium aluminate, forming sulphate. This is reduced at a higher temperature, re-forming sodium aluminate, and releasing hydrogen sulphide, which is converted to elemental sulphur in a Claus reactor. This process satisfies several criteria for a satisfactory power station process. It is a dry process, carried out without cooling the flue gas. Wet washing processes, which cool the flue gas, reduce the thermal buoyancy of the plume, and introduce the possibility of occasionally high local sulphur oxide levels. A regenerative process is preferred, since no sorbent is yet apparent which is sufficiently active for use in a hot, dry cleaning process, and yet cheap enough to discard after use. A regeneration process requires the recovery of a marketable sulphur product to offset the higher plant and operating costs involved, and on a power plant site, a process which allows recovery of elemental sulphur has advantages in terms of ease of storage and transport.

Table 1 indicates the order of magnitude of annual operating costs which have been envisaged for cleaning processes. Each estimate is sensitively dependent on assumptions made about the long term performance of catalyst or sorbent, the market value of the chemicals used and produced in the process, and the operating regime to which the electricity demand will subject the

Table 1. Estimate of annual operating cost of flue gas cleaning processes (dollars per kilowatt of plant)

	Reinluft process	alkalized alumina process	catalytic oxidation, e.g. Penelec/Monsanto† process	catalytic oxidation, e.g. Kiyoura‡ process	non-regen. limestone washing process§
gross operating cost	7.3	4.3	5.0	4.6	4.9 to 7.6
credit claimed for product sale	3.3	1.5	2.9	4.0	nil
net operating cost	4.0	2.8	2.1	0.6	4.9 to 7.6

† 3% sulphur coal; 90% plant load factor; 90% sulphur removal; costing based on 800 MW plant; credits of $20.00 per ton for sulphur, and $9.00 and $23.50 per ton respectively for sulphuric acid from catalytic oxidation and Reinluft processes.

‡ 3.6% sulphur oil; 90% plant load factor; costing based on 600 MW plant; credit of $32.20 per ton for ammonium sulphate.

§ 1.5 and 5% sulphur coal; 90% load factor; 90% sulphur removal; costing based on 120 MW plant.

chemical plant linked to the power station. It may be noted, however, that unlike the non-regenerative process, a regenerative process can produce a product which estimates suggest may actually approach in value, the operating cost of the plant.

The alkalized alumina process

A preliminary investigation indicated that a sorbent termed 'alkalized alumina' by the U.S. Bureau of Mines who had patented a route for preparing it via dawsonite ($NaAlO_2,CO_2,H_2O$), had particular value for the removal of sulphur dioxide from flue gas. The material is not stoichiometric, but the main component has been identified by its X-ray diffraction pattern as β-sodium aluminate. Its properties, when prepared from dawsonite, are distinguished from sodium

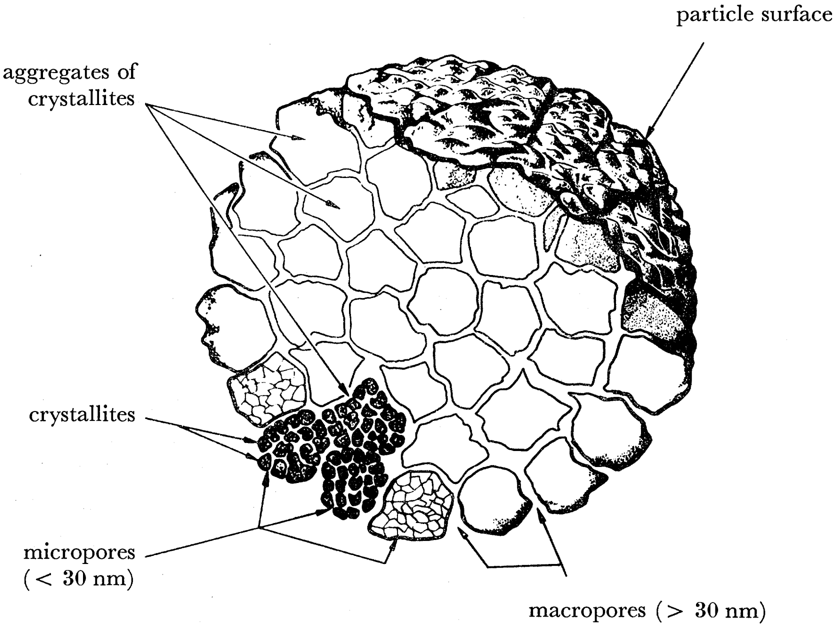


Figure 1. Diagram of the physical form of an alkalized alumina particle.

aluminate prepared in other ways by a large surface area (20 to 40 m^2/g), and smaller mean pore diameter (45 nm compared with 250 nm) and crystallite size (0.1 μm average, compared with 2.4 μm). Pore size distribution measurements give an indication of the physical nature of a particle; the greater proportion of the surface area is associated with the micropore (30 nm) structure, but the larger proportion of the pores has diameters in the narrow range of 45 to 100 nm (figure 1).

Sorption

Pure sulphur dioxide reacts with alkalized alumina at 100 °C to the extent of two monolayers, one of which can be removed by heating to 375 °C. Following this reaction by infrared spectroscopy, has shown that a layer of sulphite is formed on to which a layer of sulphur dioxide is chemisorbed (figure 2). Under dry conditions, the reaction proceeds no further, corresponding to a maximum sorption of about 3 % sulphur dioxide for a surface area of 25 m^2/g. The presence of moisture allows migration of sulphite to the interior of the crystallites with a resultant pickup of about 30 % as sulphur dioxide. An increasing proportion of sulphur is held as sulphate rather than sulphite at temperatures above 100 °C. Nitrogen oxides, present in flue gas, catalyse the exclusive formation of sulphate irrespective of temperature and increase the rate of sulphur dioxide sorption.

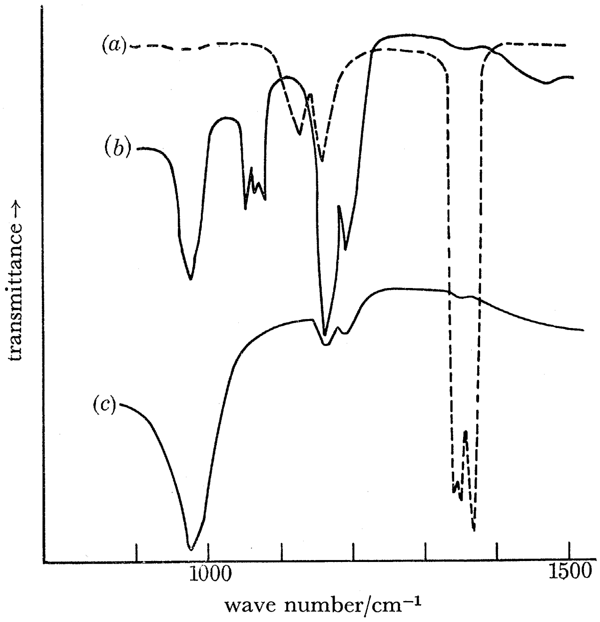


FIGURE 2. Infrared spectra of (*a*) sulphur dioxide gas, (*b*) chemisorbed sulphur dioxide and sulphite ion formed on alkalized alumina under dry conditions, and (*c*) complete conversion of the chemisorbed sulphur dioxide to sulphite ion by moisture.

The kinetics of the sorption process depend critically on the physical form of the sodium aluminate. Commercial sodium aluminate, for example, will sorb 4 % SO_2 by weight compared with 14 % SO_2 by alkalized alumina under similar conditions. Since alkalized alumina can be modified in physical characteristics over a wide range by variation in manufacturing technique, it is important to establish for any given product, the reaction rate control parameters. Kinetic studies have been made by exposing a single layer of particles to an excess of reacting gas. The sorption kinetics of one material showed no dependency on gas flow over the range 0.15 to 2.4 m/s but were dependent both on particle size and on the concentration of sulphur dioxide in the gas

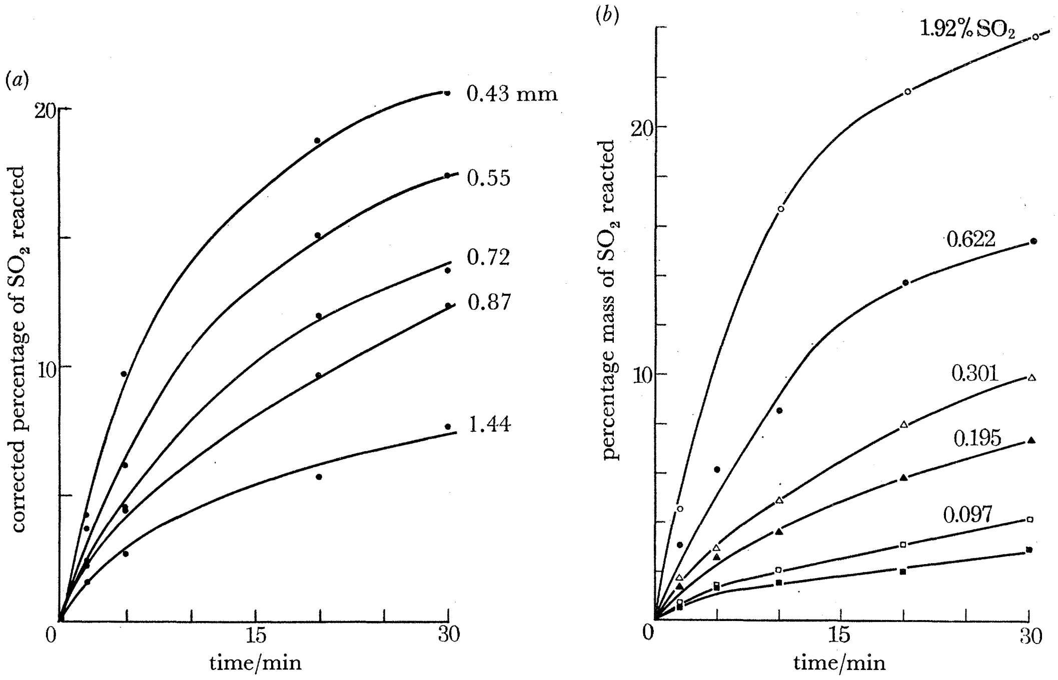


FIGURE 3. Dependence of rate of absorption of sulphur dioxide by alkalized alumina at 130 °C upon (*a*) size of the alumina particles, (*b*) concentration of sulphur dioxide in the gas phase.

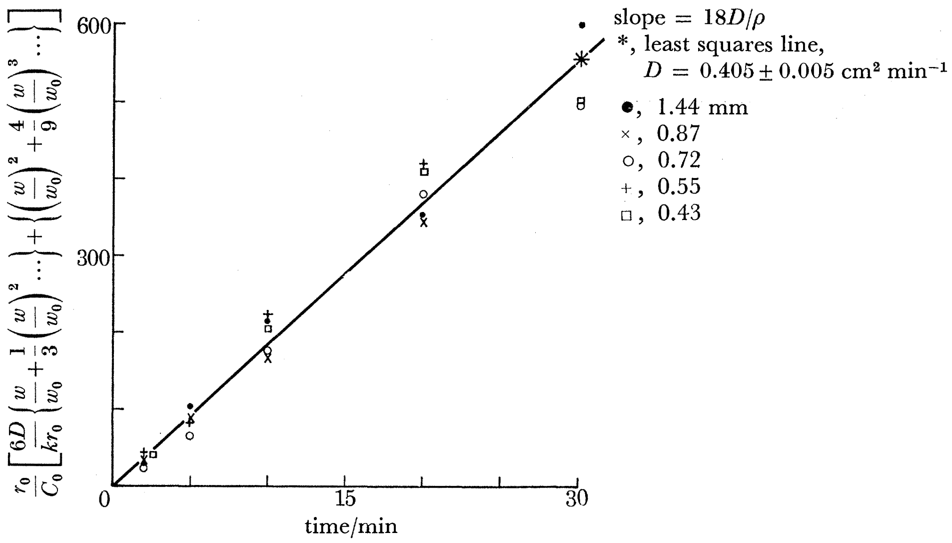


FIGURE 4. Results at constant SO_2 concentration plotted to the diffusion-surface reaction equation. W, SO_2 sorbed in time t; w_0, saturation capacity; r_0, particle radius; D, effective diffusion coefficient; k, surface reaction constant; C_0, SO_2 concentration; ρ, reaction site density.

phase (figure 3). This result suggested that boundary film diffusion was not rate controlling with this material but that pore diffusion and/or surface reaction controlled the overall process; in fact, the kinetics were found to agree with those predicted by a shrinking core model based upon control exercised jointly by pore diffusion and surface reaction (Lu 1963) (figure 4). With other materials, the shrinking core model did not apply. One variant of the manufacturing process gave a cored product in which electron probe analysis showed that only the shell was accessible to sulphur dioxide (figure 5, plate 3). Another product developed a uniform concentration of sulphur with time through the particle, in contrast to the shrinking-core mechanism previously observed. Work is in progress to establish whether the reaction is controlled chemically or by the internal surface of this material.

Regeneration

Regeneration involves the reduction of sodium sulphate; measurement of the heat of the overall reaction of sulphated alkalized alumina with hydrogen, using differential thermal analysis,

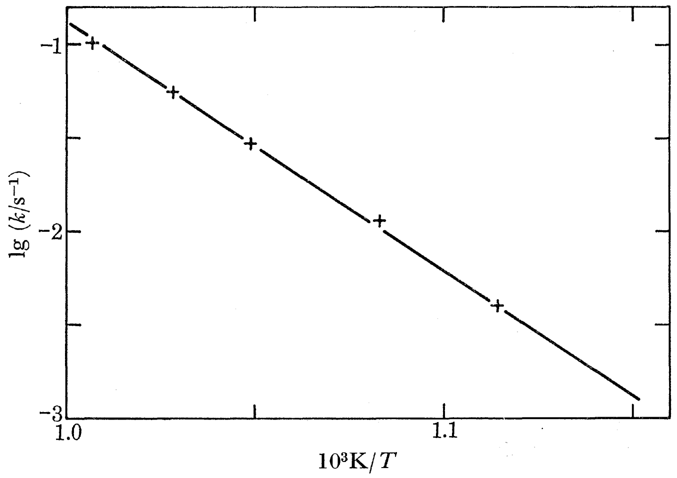


FIGURE 6. Arrhenius plot for the reduction of sulphate ion on alkalized alumina.

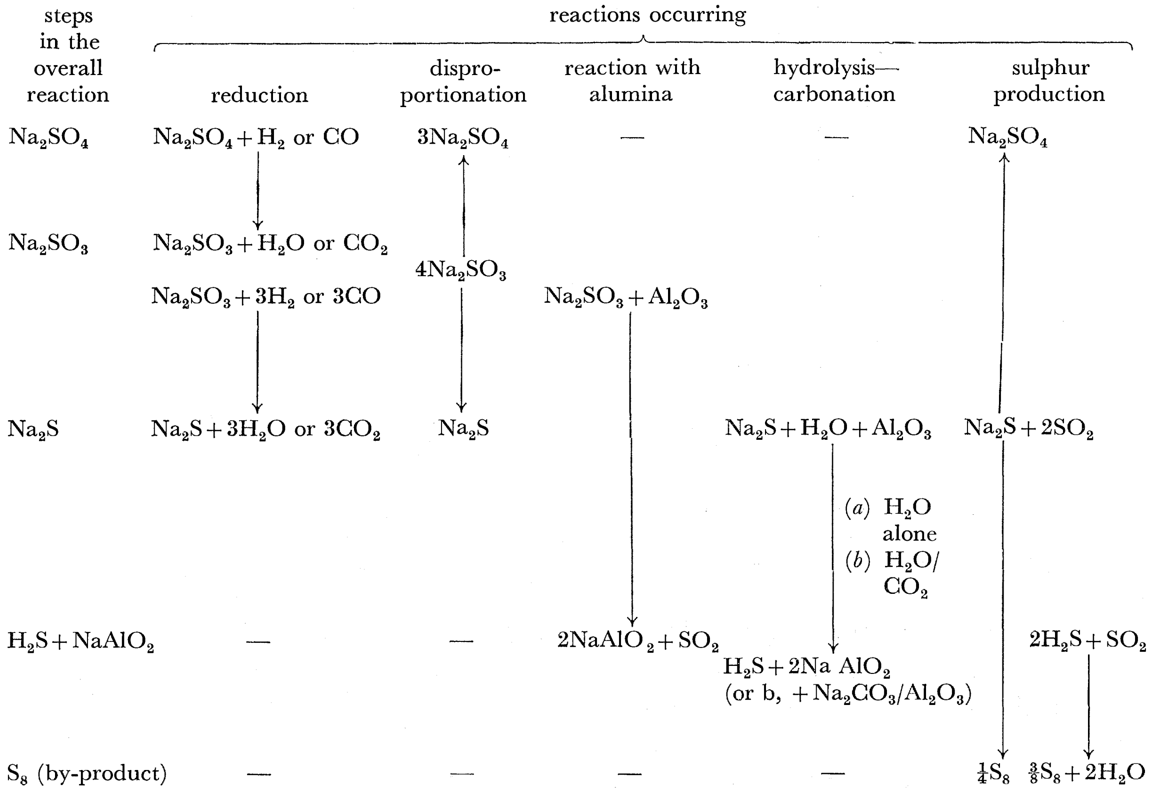
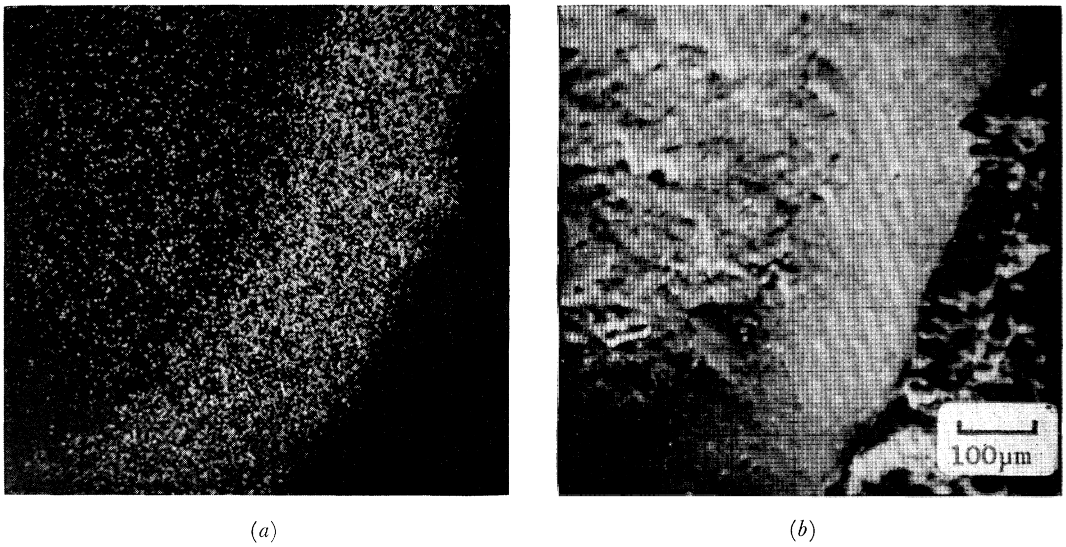


FIGURE 7. Reactions which may occur during reduction of sulphated alkalized alumina.



(*a*) (*b*)

Figure 5. Electron micrographs of part of an alkalized alumina particle section to show (*a*) preferential distribution of absorbed sulphur in the shell, (*b*) shell-core structure.

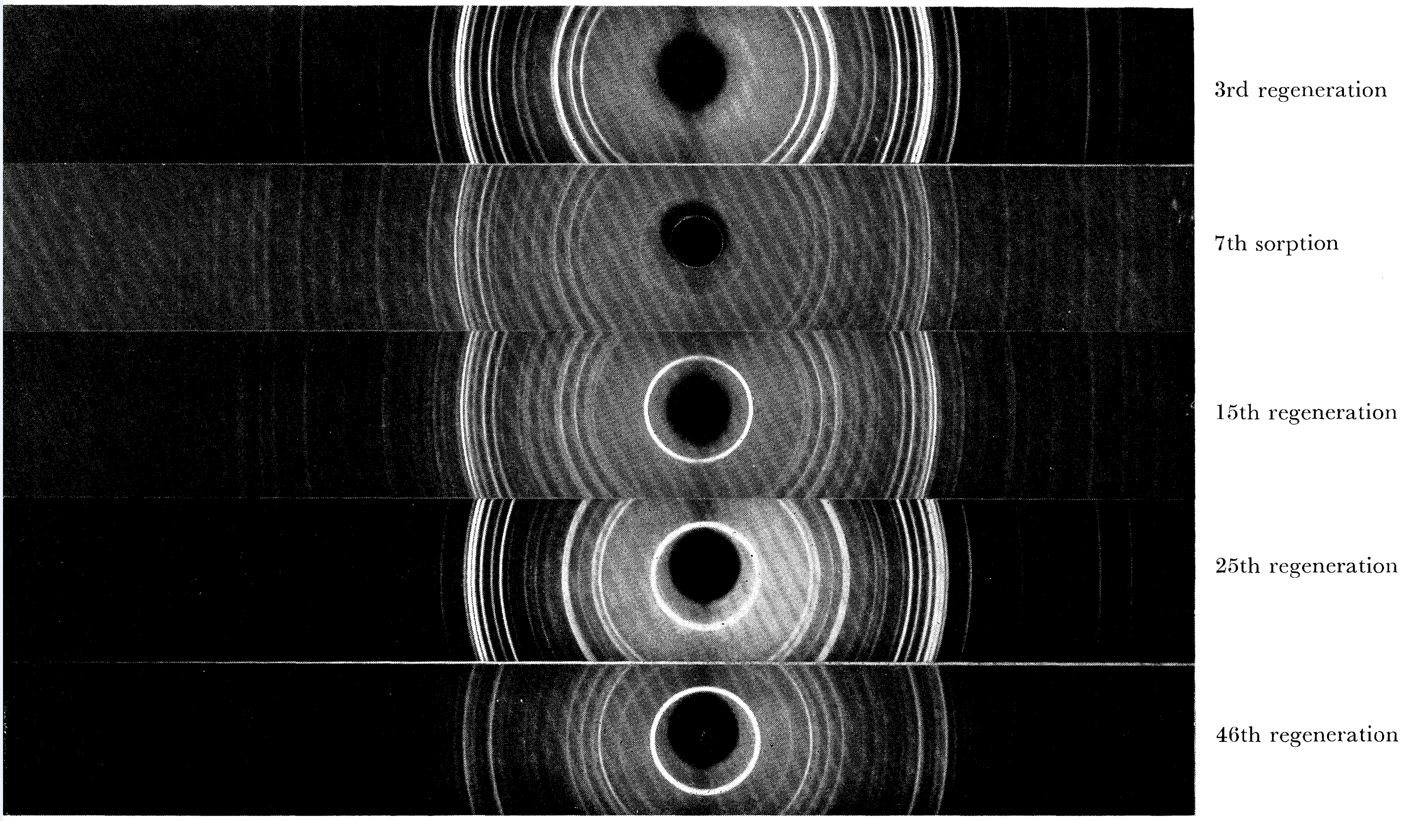


Figure 10. X-ray diffraction patterns showing development of a β-alumina phase (or $NaAl_5O_8$) during chemical cycling.

gave a value of 39 kJ/mol of sulphur removed. This value falls within the range of values calculable from available data for the reaction

$$Na_2SO_4 + Al_2O_3 + 4H_2 \rightarrow 2NaAlO_2 + 3H_2O + H_2S.$$

The rate of reduction has been studied by a technique similar to that used to follow the sorption reaction and can be expressed in terms of a first order dependence on the sulphate content. The Arrhenius plot for the reaction (figure 6) gives an activation energy of 260 kJ/mol of sulphate reduced. The rate controlling step is apparently the reduction of sulphate to sulphite

$$Na_2SO_4 + H_2 \rightarrow Na_2SO_3 + H_2O.$$

The sulphite can either disproportionate to sulphur and sulphide or react with alumina to release sulphur dioxide and re-form sodium aluminate (figure 7). Material containing mainly sulphite, on heating in nitrogen to 700 °C, is observed on subsequent analysis to contain sulphur mainly as the sulphate and the sulphide. The disproportionation reaction has been reported to be first order and the rate is significant at 617 °C (Nikitin & Kunin 1960). Some sulphur dioxide is also observed in the heating process in nitrogen, supporting the second mechanism.

The final step in the reaction is believed to involve the hydrolysis or carbonation of sodium sulphide to release hydrogen sulphide and re-form sodium aluminate. The rate of regeneration in carbon monoxide/hydrogen mixtures is faster than it is in either gas individually, and the addition of carbon dioxide to hydrogen or to carbon monoxide also improves the reduction rate.

Earlier studies on the reduction of sodium sulphate have showed that the presence of metal compounds, particularly iron, accelerate the reduction rate, and allow a decrease in regeneration temperature (I. G. Farben 1937).

Behaviour of the material on recycling

The economic viability of the process depends in large measure, on the alkalized alumina particles retaining adequate chemical and physical properties over an extensive recycling life. Some changes do occur in the early stages. Loss of micro porosity and an equivalent fall in surface area are accompanied by a decrease in total pore volume, which rapidly adopts a steady state value (figure 8). The capacity of the material for sulphur dioxide falls in a similar manner (figure 9). The porosity of the regenerated material at a given stage of cycling is greater than that of the sorbed material. X-ray diffraction has shown that long-term cycling of alkalized alumina can cause some second phase development of a form of β-alumina. Comparison with published data (Collongues, Thery & Legus 1962) suggests that this material has the formula $Na_2O.5Al_2O_3$, rather than $Na_2O.11Al_2O_3$ assigned to β-alumina. The development of this second phase is accompanied by a sodium loss which was more rapid in a second investigation where regeneration of sulphate was incomplete. It would seem that, at regeneration temperatures close to 700 °C, the non-stoichiometry which an inadequate rate of regeneration can allow, gives rise to a β-alumina (figure 10, plate 3).

Other reactive species present in flue gas can compete with sulphur dioxide for sorbent sites. About 2.5 % of carbon dioxide is sorbed over the sorption temperature range but is removed on regeneration.

Irreversible retention of chloride would be of more concern since sodium chloride is stable under the regeneration conditions. Alkalized alumina does pick up chloride irreversibly under laboratory conditions where sulphite is the main product, namely, low temperature, and absence

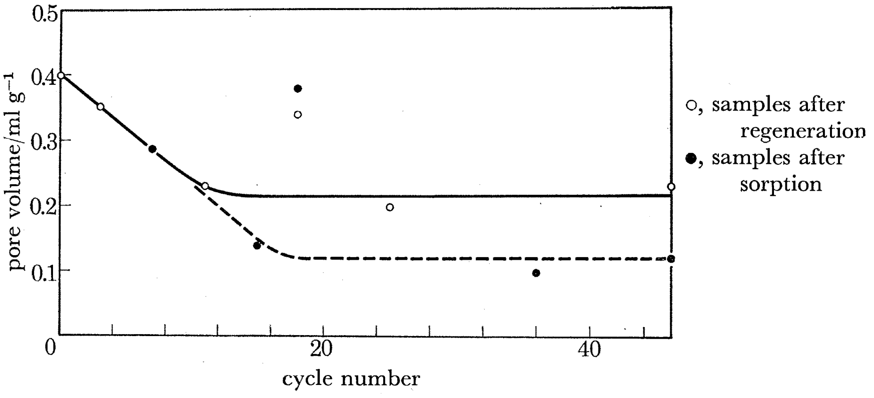


FIGURE 8. Decrease in total pore volume on chemical cycling.

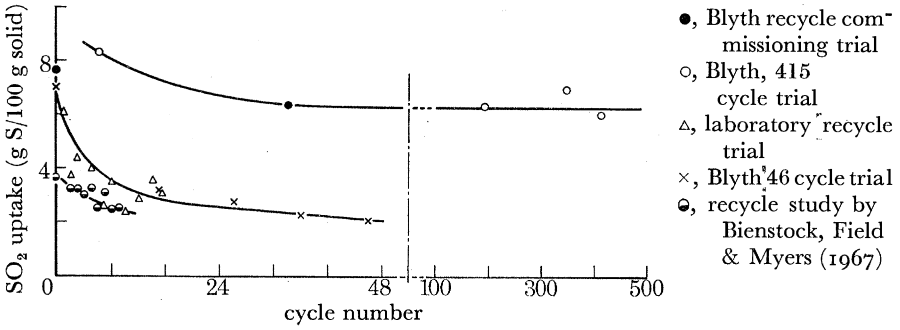


FIGURE 9. Decrease in sulphur dioxide capacity with chemical cycling.

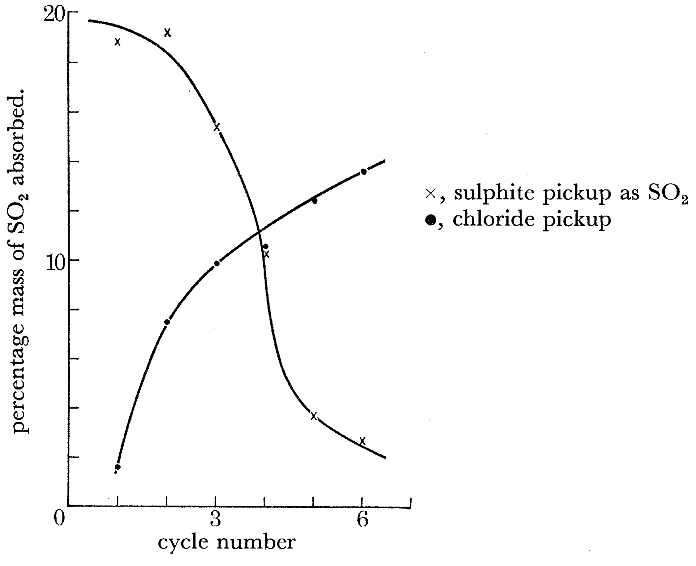


FIGURE 11. Effect of chloride ion upon the ability of alkalized alumina to absorb sulphur dioxide to form sulphite ion.

of nitrogen oxides. Figure 11 shows the consequent decrease in activity towards sulphur dioxide. Where sulphate is the main product and chloride content is low, as during exposure to power plant flue gases, no tendency for chloride accumulation sufficient to affect sulphur dioxide pickup has been found. These observations accord with the relative free energies of the reactions involved which occur in the directions shown.

$$2NaCl + SO_2 + H_2O \leftarrow 2HCl + Na_2SO_3,$$

$$2NaCl + SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow 2HCl + Na_2SO_4.$$

Plant kinetics

In addition to the kinetics of the reaction of sulphur dioxide with single particles of alkalized alumina, the behaviour of the material in chemical reactors required consideration. Studies have been carried out with two types of reactor:

(1) A fixed bed of alkalized alumina which is relevant both to sinter strand operation (i.e. a system wherein the solid rests on a belt which is drawn across the rising gas stream) and to a fixed bed reactor through which solid descends in plug flow.

(2) A batch operated fluidized bed of the solid. Data from this system is applicable to the situation where solid enters a fluidized bed reactor, and flows across the rising gas stream in plug flow.

Fixed bed reactor studies

The simple kinetic expression developed for the reaction of single particles of alkalized alumina with sulphur dioxide,

$$\mathrm{d}w/\mathrm{d}t = -kc(w_0 - w)$$

(where w_0 and w are respectively the saturation capacity of the reactant for sulphur dioxide, and the weight of sulphur dioxide reacted in t minutes; c is the sulphur dioxide concentration in the gas phase; k is the rate constant) has been used in conjunction with the mass balance requirements of a fixed bed

$$\frac{u\delta c}{\delta z} + \frac{\delta c}{\delta t} + \frac{1}{\alpha}\frac{\partial w}{\delta t} = 0,$$

where u is the superficial gas velocity, z the bed length, and α the void fraction of the bed.

These equations have been solved analytically by Amundsen (1948), using the appropriate boundary conditions, with the following result:

$$c_0/c = 1 + [\exp(-kc_0\alpha t)][\exp(kw_0 z/u) - 1],$$

where c and c_0 are the sulphur dioxide concentrations in the effluent and inlet gas streams.

The rate constant (k) measured during our fixed bed experiments was found to be in good agreement with that derived from the single particle studies.

Fluidized bed reactor studies

The penetration of sulphur dioxide through batch operated fluidized beds was measured as a function of time and correlated empirically with the principal parameters of the reactor, e.g. particle radius, bed height, gas flow rate, sulphur dioxide concentration at the inlet, giving the following expression:

$$\frac{c}{c_0} = \exp\left(-\frac{Klw}{c_0 u\alpha Rt}\right)$$

where l is the fluidized bed height, and R the radius of the sorbent particles. This expression was then used to determine the limits of reactor performance for the two ideal extremes of solid flow in a transverse flow fluidized bed. The case of ideally mixed solid requires 23 % more solid fed to the bed than the case of the ideal plug flow to perform the same removal duty. Such an increase in solids flow would lead to a larger attrition loss of solid with an increase in running cost for replacement.

The mixing characteristics of the transverse fluidized bed reactor have been established using magnetic tracer to determine the distribution of solids residence times. The model system used has a solids flow with intermediate dispersion between back mix and plug flow. Increased gas flow and solids flow at a given bed depth both increase the extent of dispersion.

The work was carried out at the Central Electricity Research Laboratories and the paper is published by permission of the Central Electricity Generating Board.

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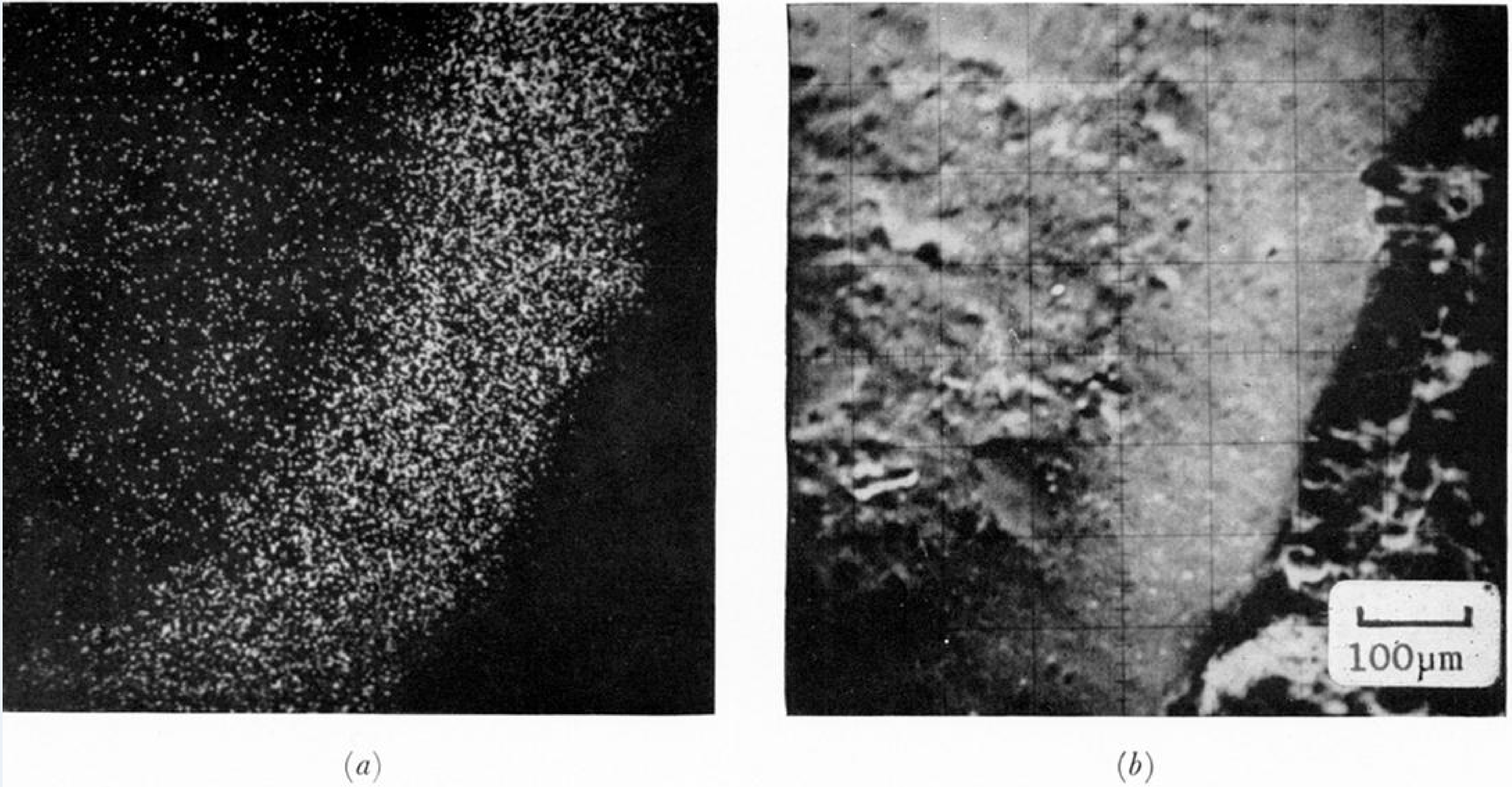
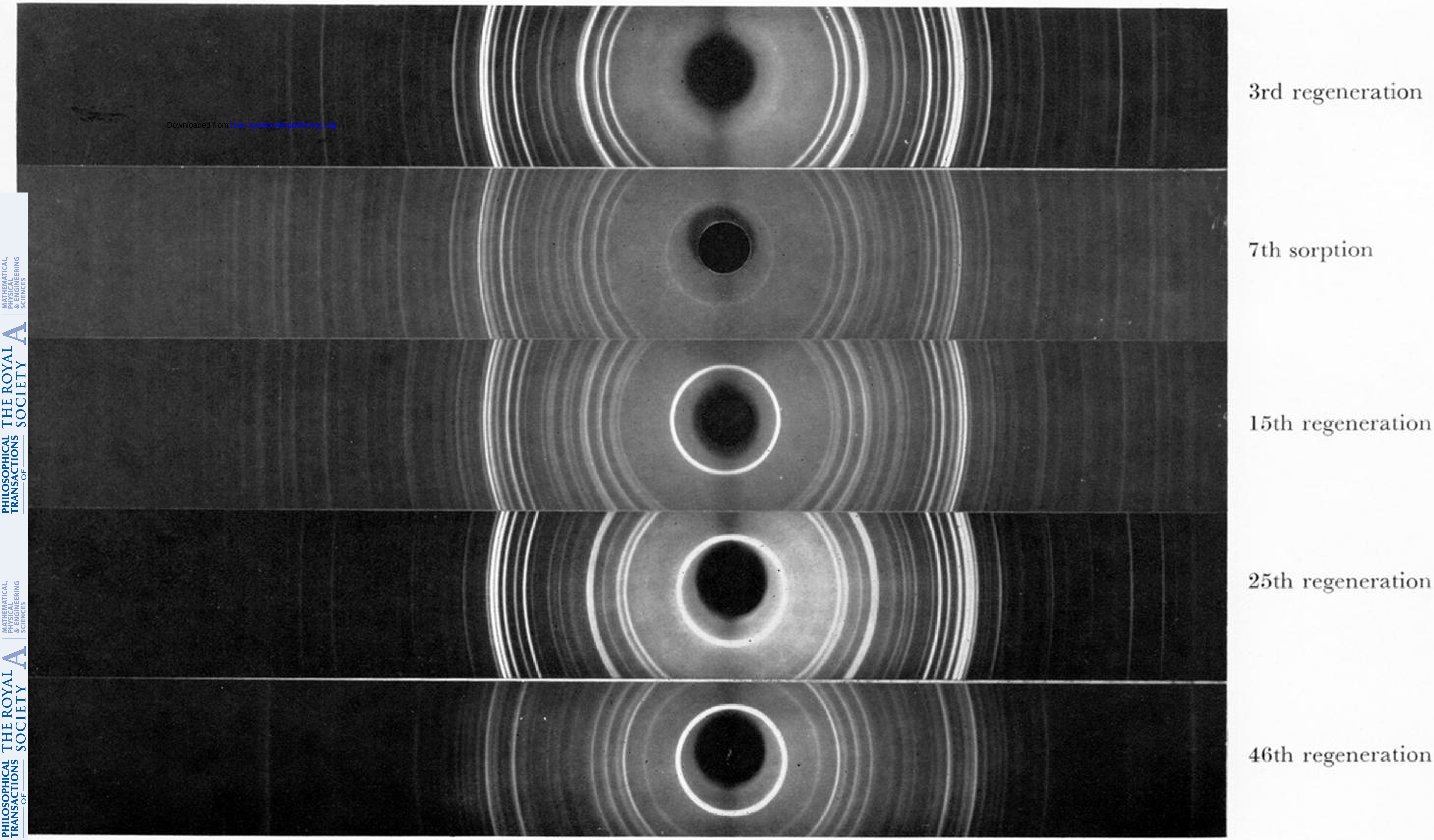


(a) (b)

IGURE 5. Electron micrographs of part of an alkalized alumina particle section to show (a) preferential distribution of absorbed sulphur in the shell, (b) shell-core structure.



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