A SHORT REVIEW

# Electrochemical methods for $SO_2$ flue gas treatment

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Electrochemical methods offer a powerful route to the reduction of pollution, and a general survey of their uses was recently published [1]. More detailed and specific aspects of the subject, such as electrochemical treatment of cyanides, phenols etc., pickle liquors from the copper or steel industries have also been written about [2–4]. Electrochemists have also considered the problems of removal of $SO_2$ from flue gases, and this paper reviews the field.

Sulphur, which occurs in almost all fossil fuels, in concentrations up to 3%, is believed to be harmful (as $SO_2$) to man. A measure of doubt still exists here, in that it is possible that it is harmful only in the presence of particulate matter such as carbon particles. However, its deleterious effects on all sorts of materials and machinery, especially ironwork and stonework, is undisputed. A considerable effort has been devoted to the elimination of this sulphur from flue gases and review articles of the major processes have been written by Newell [5], Cortelyou [6] and Slack [7]. Two points in the general sense should be made. Firstly, the removal of sulphur is of necessity an added cost. It is often stated that the sale of the recovered sulphur can offset the extra costs. This is true only insofar as it is remembered that the amount of sulphur emitted from large plants alone vastly exceeds world sulphur consumption. Thus while some operators may indeed recover and market their sulphur, not all can do so, and the resultant competition will obviously affect the market price for such recovered sulphur. Until recently, it has been stated that sulphur can be removed either before or after the combustion process. The main emphasis has been on the latter method, for

reasons which are understandable, especially where solid fuels are concerned. In the last year or so, work has been done on combustion in fluidized beds, using both oil [8] and solid fuels. The Esso Research Laboratories at Abingdon, Berks, and the Coal Board who, respectively, have pursued this, now believe that sulphur removal during combustion is also feasible. It is clear that such a solution, or a prior desulphurization of fuel, eliminates the problems of handling large volumes of hot gases where cooling is undesirable.

**Electrochemical methods of flue gas scrubbing**

A number of patents, publications and press releases describe electrochemical methods for flue gas washing. All would appear to be based on washing the gases with a liquor which is then treated electrochemically. This also cools the gases and so may require additional forced draught equipment, though after scrubbing and precipitation, a much lower stack may be acceptable. Most of the processes reviewed in [5–7] are not electrochemical and some of these use solid scrubbing materials, which operate at far higher gas temperatures and reduce the cooling problem. An advantage common to all electrochemical methods is that the wash-liquor may be stored in large tanks to be treated during off-peak hours when the price of electricity at the power station is governed by marginal operations and the price of the fuel, which may be as little as 0·12 p/kWh, depending on the costing convention employed. The main methods will now be considered in turn.

## (a) *Stone Webster/Ionics method*

This process is the most fully developed of all the electrolytic methods, and according to [9, 10] in which the process is described, a pilot plant has operated during the latter half of 1967 at Gannon Power Station, one of the Tampa Electric Group, in Florida. The process operates as follows:

Sulphur dioxide is scrubbed with caustic wash liquor

$$NaOH + SO_2 = NaHSO_3$$
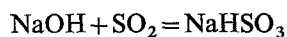
and the bisulphite is passed to a second tower, where, mixed with sodium bisulphate, it is heated by steam-jacketed tubes to give:

$$NaHSO_3 + NaHSO_4 = Na_2SO_4 + H_2O + SO_2$$
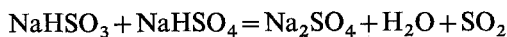
The heart of the process is the electrodialysis cell, which converts sodium sulphate solution to sulphuric acid, hydrogen, sodium bisulphate and caustic soda and oxygen. The acid stream goes to a neighbouring plant where it is enriched by the $SO_2$ piped in from the steam-heated tower, having first been oxidized to $SO_3$ in a contact vessel. The caustic recirculates to the scrubbing tower, the bisulphate to the steam-heated tower. The gases hydrogen and oxygen are presumably saleable. From an electrochemical point of view, the cell is of interest since it appears to be the first time that sodium sulphate solutions have been electrolysed to give three liquid streams. During the war, a series of plants were operated to recover caustic soda and sulphuric acid from waste liquors in the rayon viscose industries, and these plants, using mercury cathodes, Pb/Ag anodes ('Tainton anodes') and diaphragms of rubberized canvas or similar materials are described in [11]. Presumably, by suitable mixing of the acid and alkali streams, they too could be engineered to give caustic, acid and bisulphate as well. However, the current trend is not favourable to mercury cells, for reasons of contamination by the metal. Process economics are given in [9, 10] by the manufacturers of the process. It is clear that, as quoted, the process would not be viable under open commercial conditions, In the event of a subsidy being allowable for the anti-pollution plant, the process is in the same cost bracket as other non-electrochemical methods. However, the fact that no further information has been released by the manufacturers, in spite of direct approaches, must imply its own conclusions.

## (b) *Pintsch-Bamag process*

British Patent 950,204 (to Pintsch Bamag) discloses a method very similar to the Stone-Webster/Ionics in that it employs caustic soda wash-liquor and an ion-exchange membrane equipped cell. In this process it is clear that not only the $SO_2$ but also the $CO_2$ is scrubbed out and the latter gas is expelled as the wash-liquor becomes more acid during the electrolysis stage. What happens to the $CO_2$ in the Stone-Webster process is not stated, but it is presumably released when the bisulphite is formed. The patent describes the Pintsch-Bamag cell, which is unusual in that it is fitted with two cationic membranes. In one form, it also has a mercury cathode. The spent wash-liquor is fed into the central compartment, and sodium and hydrogen ions migrate through one of the cation membranes. Hydrogen is discharged at the mercury cathode, while sodium amalgamates with it. The mercury/amalgam is circulated in the same way as the normal chlorine cell, being treated with water in a separate 'denuder' vessel to give caustic soda, which is returned to the scrubbing tower, and clean mercury, which returns to the cell. Loss of sodium ions from the central compartment of the cell lowers the pH so that $SO_2$, $CO_2$ etc. are given off. Hydrogen ions are replaced by migration from the anode chamber, which is fed with water, and where oxygen is evolved at the anode. The patent, which also shows a two-compartment cell, claims that addition agents, such as amino acids or arsenious acid, can thus be continuously recirculated round the process without being electrochemically oxidized. By comparison with the Stone Webster, the economics of the process must be similar, though perhaps rather more expensive to account for capital charges in the mercury inventory. There is no evidence that the process was ever operated on a significant scale, and an approach to the manufacturers has not elicited any further information.

## (c) *The Simon-Carves process*

This process is disclosed in British Patent 930,584 (to Simon Carves Ltd) and differs completely from the previously described approaches. The flue gases are first scrubbed with sulphuric acid, and after electrolysis, the product is persulphuric acid which leads to hydrogen peroxide or the per-salts. The problems associated with the corrosive nature of the 40–80% sulphuric acid which is mentioned in the patent must be formidable, and the actual kinetics of the process are not fully discussed. The sulphuric acid also contains hydrogen peroxide and persulphuric acid, the latter compounds causing the $SO_2$ to be oxidized to $SO_3$ which dissolves in the acid. The latter, now stronger in $H_2SO_4$ and leaner in $H_2O_2$ and persulphuric acid, is passed to an electrolysis cell of the type used to manufacture per-acids electrochemically (such cells are described in [11]). Yet another problem must arise from the heat exchange equipment. The entire 'moving-burden' of acid and per-acid has to be alternately heated up to flue gas-temperature (in the scrubbing tower) and cooled (in separate coolers) before the electrolysis stage can commence. Commercial practice shows that the electrolysis operates best at 15°C or even below. The cost of such heat exchange equipment in acid-resisting metals is not negligible. There is no indication of the efficiency of the scrubbing process. A spontaneous thermal decomposition of the hydrogen peroxide to form water and oxygen (either in the gas phase or catalytically on solid surfaces) as well as the per-acids would be expected, and this would lower the efficiency of the system. Once again, no evidence exists that the process was ever scaled up.

## (d) *The Lockheed process*

A press release [12] revealed that Lockheed were working on an electrochemical method of flue gas scrubbing, using a bed electrode. No further information was released, and a recent approach to the company brought the answer that the project had gone into abeyance because of shortage of funds.

## Discussion

This survey of published methods for electrochemical flue-gas washing may not seem encouraging, yet it should be read in the overall context of the problem where no one solution has emerged as being preferable. It may well be that on a factory scale, which is the only one where something approaching economic recovery could be practised, electrochemical methods do not prove the best. However, there is also the problem of emission from domestic chimneys. In this case, a different set of economics operate, and convenience factors may override purely financial ones. The small height of the domestic chimney makes it a far more important source of pollution than the high factory chimneys. In addition, the geometry of the system is different, with a much lower gas flow : orifice area than the industrial chimney. An electrochemical device for removal of $SO_2$ here, provided it was convenient to install, maintain and operate, would certainly be of the greatest value. Rough calculations show that it would not be impossible to fit, within the domestic chimney itself, a cell to oxidize $SO_2$ to $SO_3$ and to wash this down into a separate drain to earth. The oxidation might be accomplished using any of the principles outlined above, or others, such as the electrochemical generation of $H_2O_2$ by reduction of air, as described in [11]. In another configuration, $SO_2$ could be oxidized to $SO_3$ and air could be reduced at the cathode. The poor solubility of $SO_2$ in acid media could be partially overcome by use of a matrix type of cell. Much data already exists regarding the kinetics of $SO_2$ electro-oxidation, and this is found in [13], with additional work described in [14, 15].

The suggestion has also been made that electrochemical methods be used to remove sulphur from fuel oil. Clearly electrochemical processes in the hydrocarbon itself are not possible. The suggestion was for sodium metal to be used to extract sulphur and the sodium then to be regenerated. This idea presents at least one difficulty common to reactions in liquid/solid systems, namely that the sodium sulphide forming on the metal itself will 'passivate' it and prevent further reaction. Secondly,

from an energetic standpoint, the idea is similar to the Moss (non-electrochemical) process [8], with the drawback that the energy required for decomposition of sodium sulphide is far greater than the (only thermal) energy required to convert the $CaSO_4$ or CaS back to CaO in the Moss process. It is always possible that a solvent extraction process is developed in which the sulphur is extracted from the fuel oil, and electrochemically removed from the extraction solvent. This certainly appears to be the direction in which the laboratory electrochemist must apply his thoughts.

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