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APPENDIX 11

The Removal of Dissolved Salts from Recirculating Waters in the Vaal River Drainage System

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ABSTRACT

The Vaal River system is the most important water supply area in South Africa. A substantial amount of water is recycled in the systems and this leads to a high TDS level. Mine pump and process waters contribute 25 % of the TDS load in a small fraction of the circulating flow.

It is proposed to remove the TDS from such waters by precipitation with barium carbonate. Sludges generated from the water precipitation process would then be treated in a central facility to regenerate barium carbonate, producing sulphur and slaked lime as by-products. This facility could advantageously be integrated with the operating of a large power station.

The efficiency of such a scheme on the water quality in the Vaal area could be equivalent to that obtained through increased inflow via the Lesotho Highlands Scheme.

Not many people now remember the alarm that greeted the publication of a small book "The Limits to Growth"(1) which pointed out the consequences of exponential growth of population and industry, in a world of finite resources. Partly, this is because the world economy came off the exponential curve within a year of publication owing to the oil crisis, and the Western World then became concerned more with the consequences of negative growth; and partly because prophets of gloom never enjoy sustained popularity.

Nevertheless, the basic tenets of the authors' thesis are undeniably true; their predictions are simply inaccurate in time-scale.

Curiously the supply of fresh water was not one of the resources considered by the above authors; in South Africa this is *the* resource which could within in a few years place limits on growth. The region is already water-short; over 60 % of the mean annual run-off is already utilised, and this almost exclusively by the 25 % of the population with Western standards of living. Quite obviously it will not be possible to raise the standard of living of even our existing population to Western standards, let alone cope with a steadily increasing one, without radical alterations to the pattern of water usage.

The traditional response to insufficient water is the construction of new impoundments but this approach is essentially short-term in nature. In the longer term the cost of harnessing new water resources can be expected to increase exponentially as the closer and more suitable dam sites are utilised. The only "permanent" solution to the problem is thus the large-scale recycling of water, since most large users (other than agricultural) do not consume the supply but merely contaminate it with organic and inorganic materials.

Large-scale recycling of water is in fact already taking place, especially in the inland regions of South Africa, but in an uncontrolled and inefficient fashion. At best, the recycled water has been treated in a conventional sewage works which removes only the bulk of the organic matter. Dissolved salts (TDS) are not removed and build up in the recirculating system. This lowers the quality of the water and has a large cost associated with problems caused by increased scaling, corrosion, increased requirements of detergents, deleterious effects on crops etc.

A major example of a large recirculation system is provided by the Vaal River system. This is the most important water supply area in South Africa, providing water to 42 % of the urban population of the Republic and contributing to 77 % of the country's mining output, 58 % of the total industrial production and 44 % of agricultural production (2).

By the year 2010 the water demand in the region will have increased to nearly 4 billion kilolitres per annum (3). At the same time the water quality in the area is deteriorating with the TDS level in the Vaal dam rising at an annual rate of 2,5 mg/ℓ (4). In 1980 the level had already reached 150 mg/ℓ, but in the Vaal Barrage region the SABS recommended maximum TDS level of 455 mg/ℓ is already being exceeded regularly. The economic cost of this increase in TDS is large ; it has been estimated that an increase in TDS from the 1980 levels to 800 mg/ℓ will cost the community over R 200 m per year(5).

When viewed in this context, the construction of large water schemes, such as the Lesotho Highlands scheme, can be seen as not primarily aimed at augmenting water supplies. Rather, this water will be used to dilute the TDS of the existing supply to acceptable levels, and to provide a medium by which excess TDS load may be flushed down to the sea. The alternative approach, to control the level of TDS in the recirculation system by inserting an effective removal step, addresses the problem more directly and has the advantage of being subject to the laws of science and not the vagaries of nature.

The most direct approach is to attempt to eliminate the root causes leading to the contamination of the water supply. This is obviously most easily done if the sources of contamination are confined to relatively few points.

Major point sources in the Vaal River System are mine pump and process waters. A number of techniques have been investigated in efforts to reduce the large TDS load which is picked up by these waters. While good technical progress has been made, it is clear that the cost of doing this will be high, and it could in fact be more effective to remove the dissolved salts from the contaminated water afterwards.

The ease with which TDS can be removed from the recirculating water depends greatly on the nature of the inorganic constituents ; Na^+ and Cl^- are intractable constituents for which no economic technology exists in this context while Ca^{2+}, Mg^{2+} and SO_4^{2-} are by comparison removed rather easily. Fortunately the major constituents of the TDS load entering the Vaal system are in the latter category, and the prospects for economic control of TDS are correspondingly increased.

A number of technologies for the removal of TDS from water of composition corresponding to those entering of Vaal system are either already commercially available or under development in South Africa. These include -:

- Ion exchange which is used where a particularly high quality water is required but the process is not suitable for high volume applications.
- Electrodialysis which has been tested on mine and power station cooling waters but found to be too expensive for large scale operation.
- Seeded slurry reverse osmosis, a variant of the established technology, designed to operate on waters where insoluble material such as gypsum will precipitate on concentration. This is under development by the Chamber of Mines and appears to be an effective but somewhat costly technique, quite different in the level of sophistication to the kind of technology traditionally used in large-scale water treatment.
- Biological processes which have received extensive investigation by the CSIR. These also involve complex flow sheets and do not appear to economically viable at this stage.

The disadvantages of these technologies have lead a number of workers in South Africa to propose the use of the simple and well-known chemical precipitation route, using a barium salt to remove sulphate, simultaneously converting Ca^{2+} and Mg^{2+} into insoluble components. The principal advantage of the technique is its simplicity which is compatible with large scale applications on unsophisticated plants. This application is however complicated by a number of factors among which are the high cost of suitable barium compounds and the high toxicity of soluble barium salts.

In our view, the second factor rules out the use of compounds such as barium sulphide which have been proposed for this application;(6) no matter what safeguards are built in, the risk of overdosing in the context of a large, unsophisticated treatment facility is simply too great. This problem can be overcome by using a barium salt of very limited solubility, such as $BaCO_3$ so that even large dosing errors could not result in an acute toxicity problem.

The stoichiometry of TDS removal using barium carbonate is extremely simple ;

$$BaCO_3 + CaSO_4 \rightarrow CaCO_3 ,$$

both reaction products being extremely insoluble.

Thermodynamically the equilibrium in this reaction is far to the right, even though $BaCO_3$ is itself almost insoluble. However, the reaction of an insoluble substance with a dilute solution to form a more insoluble substance could be expected to be very slow. Indeed a previous worker (7) identified this as a major technological problem to be overcome, as far back as 1972.

More recently Maree *et al* (8) have reported results obtained in a joint investigation by the CSIR and Anglo-American Research Laboratories. They found very slow reaction rates; 16 x stoichiometry being required to achieve a realistic rate of sulphate removal. They ascribed this to a slow, rate-limiting step of dissolution of $BaCO_3$, the rate of this step being dependent on the surface area of the $BaCO_3$ crystals.

To overcome this, they have suggested a system in which the contaminated water is recirculated through a fluidised bed of barium carbonate particles. This would provide the high interfacial area necessary to give an acceptable rate of sulphate removal while reducing the consumption of $BaCO_3$ to somewhere near the stoichiometric requirement.

In a separate investigation at the University of Natal, Trusler (9) also studied the kinetics of sulphate removal with $BaCO_3$. His results appear to be in complete contradiction of those of Maree, showing rapid precipitation even at the stoichiometric level and only a small effect of the addition of excess reagent. This apparent contradiction is resolved by noting that $BaCO_3$ particles of very different sizes were used in the two investigations. Trusler used particles of around 5 μm in diameter; while Maree does not quote the crystal size used in his experiments, rough calculations based on both kinetic and hydrodynamic considerations indicate that his particles must be around 100 μm in diameter.

The problem of slow reaction rate can therefore also be overcome by using a reagent of high enough specific surface area, i.e. a small particle size. It will be possible to control the particle size of the reagent during the manufacturing process, but if necessary, the surface area could be increased by wet milling the product in a stirred ball mill prior to use(10).

The milled product could then be dosed to a simple conventional water treatment plant in roughly stoichiometric amounts.

Trusler found that the kinetics of sulphate removal are also affected by the nature of the cations in solution. If sulphate is present as sodium and magnesium sulphates in addition to the usually dominant $CaSO_4$, the precipitation of sulphate is greatly retarded. He showed that this could be overcome by adding hydrated lime in stoichiometric proportion to the sulphate present in excess of Ca^{2+} ions in solution. This result has been theoretically verified by Loewenthal(11). In tests using both synthetic and real high sulphate water, virtually complete removal of SO_4^{2-} Ca^{2+} and Mg^{2+} was achieved, leaving only the intractables Na^+ and Cl^- in solution.

From a technical point of view, barium carbonate precipitation is thus simple and attractive. The compound unfortunately does not occur naturally in economic quantities and must be manufactured from barytes. South Africa has large deposits of this mineral but these are located at some distance from the PWV area. However, the same technology that is commercially employed for the treatment of barytes could also be used to regenerate $BaCO_3$ for recycle from the sludge formed by treating sulphate rich waters.

The regeneration process involves the thermal decomposition of $BaSO_4$ under reducing conditions to form BaS. This is highly soluble in water but is easily decomposed by CO_2 to precipitate $BaCO_3$, forming a by-product of H_2S. H_2S can then be converted into elemental sulphur by several commercial processes, and this is a convenient and valuable by-product. The end result of a combined TDS removal and barium recycle process is thus the formation of a purified water stream, with sulphur and a slaked lime sludge as by products. Coal is the only reagent consumed in the process.

Our concept for the application of this technology is thus the treatment of sulphate-containing waters in simple low-cost facilities at convenient locations. The sludge formed at each treatment plant would be transported to a central facility where a suitable $BaCO_3$ reagent would be regenerated and the various by-products recovered.

The most effective points at which the water-treatment facilities could be located are the large mines in the area that generate significant volumes of highly contaminated water. It has been estimated (12) that these sources generate a total flow of 200 Mℓ/day which contains 25 % of the TDS load entering the Vaal System. Removal of this TDS load would have a significant impact on the whole system - it would be equivalent to increasing the inflow of high-quality water into the system by 30 - 40 %. An increase of this magnitude would be a major undertaking similar in size to the Lesotho Highlands project.

The water product from such installations would be of high quality, better in fact than that supplied by the RWB to industrial consumers in the region. It would be wasteful to allow this water to simply drain back into the Vaal Dam when it could be supplied to consumers requiring high quality water.

There are a number of such potential consumers in the region; some of the most important are the directly cooled power stations. These require large volumes of high quality cooling water. This water is evaporated, and in order to contain corrosion and scaling problems a low TDS in the make-up water is required, and considerable capital has to be invested to control TDS build-up. Mine-water treated by barium carbonate would be well-suited to this application.

Integration of this desalination scheme with a power station would have a number of subsidiary advantages :-

1) Power stations are substantial consumers of sulphur, a major by product of the process. This is converted to SO_3 which is used to increase the conductivity of the stack gas and thus increase the efficiency of electrostatic precipitation of fly-ash.

2) Many of the facilities required for the barium carbonate regeneration process are located on-site at power stations. These include coal handling facilities, steam and power, well-equipped laboratories, well-designed sludge disposal facilities etc.

In conclusion it appears to us inevitable that control of TDS build-up in the Vaal water system will be introduced. The advantage of the particular scheme presented above is the simplicity of the water treatment process. This is however offset by the complexity and probable high capital cost of the regeneration process. By integrating the scheme with the needs of a large consumer such as Eskom the overall capital and operating costs could be reduced considerably.

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