Metals, muck, and magnets

Raw water is mixed with magnetite in a train of three contact tanks.

Newton's apple and Archimedes' bath are familiar examples of the part lateral thinking — the ability to make two plus two equal five — plays in science and discovery. The development of magnetic methods of water purification provides some more examples.

In the early 1970s, CSIRO scientists investigating the desalination of drinking water developed unique ion-exchange resins — chemically reactive beads — capable of removing salt from brackish water at ordinary temperatures and releasing it when they were washed with hot water.

There are many places in Australia where brackish water supplies would benefit from such a process, but the uptake of salt by the resins was too slow. For the Sirotherm process as it was called (see *Ecos* 2) to be practicable, it would have to be speeded up. Smaller resin beads would take up the salt faster, but they were too difficult to handle: they would be too easily washed away, or very high pressure would be needed to force water between them.

One of the inventors of the Sirotherm process, Dr Don Weiss, recalled that when magnetic particles such as iron filings are magnetised they collect in clumps and wavy lines, with spaces between the lines. Thinking laterally, he reasoned that incorporating magnetic material into fine Sirotherm beads would make them stick together so they would not wash away, while at the same time leaving spaces between them so water could pass through easily.

Ion-exchange resins containing *gamma* iron oxide showed just these properties — and offered an additional, unexpected benefit: because of the water-filled spaces between them the beads could pass through a pump without being destroyed, as conventional resin beads would be. This meant ion exchange could be continuous: resin could be loaded with salt in one column, then pumped to a second column where the salt was stripped off so the resin could be returned to the first column to purify more water... and so on.

Any old ions

The idea of using magnetic beads was not limited to Sirotherm, however. Ion exchange can also be employed to remove other soluble impurities, such as hardness or coloured organic matter from drinking water and toxic heavy metals from industrial waste-water.

Dr Brian Bolto, Dr David Dixon, and Dr Rob Eldridge, of the Division of Chemicals and Polymers, tailored ion-exchange beads for such applications, using fine beads for rapid purification with *gamma* iron oxide (or, potentially, some other magnetic material) to provide an invisible 'handle' so they could be moved about at will. And, because the beads can be designed to select a particular impurity according to its electrical charge or other chemical properties, metals such as mercury or nickel can be removed selectively and returned to an industrial process.

Dr Dixon and his colleagues used magnetic resins to soften hard water for drinking and to remove zinc from metallurgical waste-water. Dr Eldridge demonstrated that a similar resin could treat waste-water from metal-finishing processes, and recover both the now-cleaned water and its metal content. Suspended solid matter, which would rapidly block a column of conventional resin, is no problem to the constantly moving magnetic ion exchanger.

Removal of insoluble impurities from drinking water requires a cheaper material than magnetic resin. The elegant solution was to use iron oxide without any resin coating; the SIROFLOC process (see *Ecos* 31) employs magnetite.

Dr Weiss and his fellow researchers noted that the impurities in raw (untreated) water carry a negative electrical charge and, thinking laterally again, reasoned that slightly acidifying the water would create a positive charge on the surface of the magnetite and cause the impurities to adsorb — that is, stick to the surface of the magnetite particles. The charge could then be reversed by adding an alkali, causing the magnetite to shed its load and enabling it to be re-used.

SIROFLOC is now used on a commercial scale for drinking-water purification at Mirrabooka (Perth, W.A.), Bell Bay (Tas.), and Redmires (Yorkshire, U.K.), and in Taiwan. The magnetic resin and SIROFLOC processes are described in further detail in the accompanying box.

Cleaning up sewage...

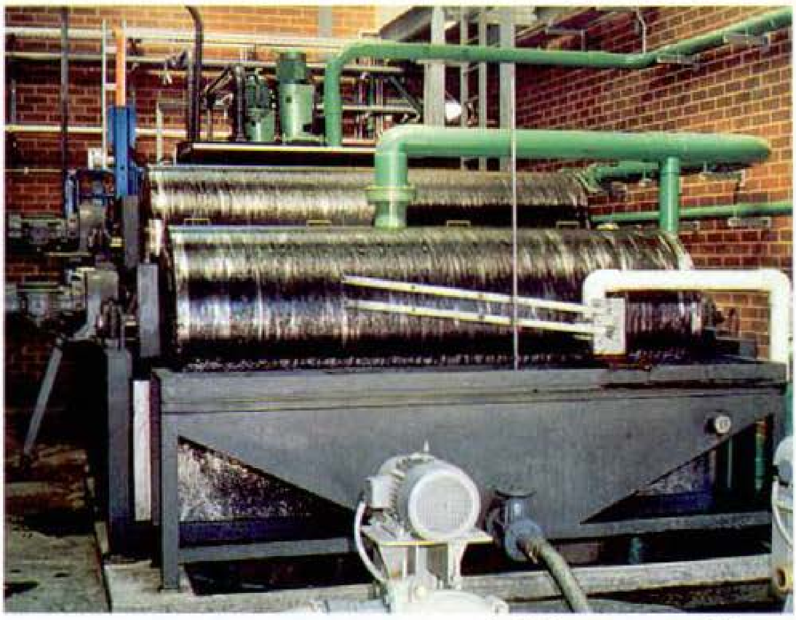
In the early 1980s, CSIRO researchers began investigating the use of SIROFLOC for sewage treatment. Domestic and industrial sewage is either dumped at sea (a practice that has spawned growing opposition as well as environmental problems) or treated with biological techniques that convert organic matter into sludge that is difficult to dispose of in an environmentally acceptable manner.

SIROFLOC promises cost savings in sewage treatment plants similar to those it has already delivered in water purification, and pilot-scale trials are under way at CSIRO's facility at Lower Plenty, Vic., and the Sydney Water Board's Malabar treatment plant. Results from these trials are encouraging: the process is efficient, producing only a small volume of sludge and realising significant savings not only in equipment but in the cost of basic materials (magnetite, for example, is so cheap that in Australia 80–90% of its cost lies in transportation.

... and recycling metals

More recently, SIROFLOC's applications have been expanded again: the magnetite process, as it is now known, is being used to extract metals from mining and industrial waste-waters. Traditional metal-extraction processes such as precipitation are uneconomically slow, wasteful, and unselective; other techniques offer too few advantages over precipitation.

Dr Dixon used SIROFLOC's ability to remove ions such as iron, aluminium, and zinc through chemical manipulation of the waste-water to develop a system that is faster, more cost-efficient, and environmentally safe.



Top: Water cleaned by the SIROFLOC process is stored in clarifying tanks. *Lower*: Magnetic drum separators strip impurities from the magnetite.

The approach is basically the same as that used for drinking water, except that magnetite particles are fed into a waste-water solution that has been adjusted to a nominated pH. At the invitation of Denehurst Pty Ltd, he set up an experimental magnetite plant at the firm's Woodlawn mine near Canberra to remove unwanted iron and aluminium from a zinc-rich solution. In a subsequent trial with another mill stream, magnetite was used at a higher pH to remove copper and zinc ions as well as iron and aluminium, to produce an essentially metal-free water for use on the mine site. The magnetite is regenerated and concentrated effluent pumped into evaporation ponds.

The trials were a success, and Dr Dixon feels the process could be applied to other mining and industrial applications. The Woodlawn trial operation was set up to run at a pH of 6·0, but has worked successfully at pH 8·0 and 10·0.

Dr Dixon has also been working on a collaborative venture with Dr Graham Sparrow of the Division of Mineral Products to remove iron ions from water leached from the pressure oxidation of a complex copper–lead–tin ore. In the case of unwanted metals, after the magnetite has been regenerated by acid or alkali the concentrated effluent is pumped to evaporation ponds (which, since the solution is highly concentrated, occupy less space than would be needed in other methods) for disposal. If the metal ions are to be recovered, the concentrated effluent is treated — for example, by reverse osmosis — before the metal is extracted. In either case, the end products consist solely of highly concentrated effluent, for recovery or safe disposal, and clean water.

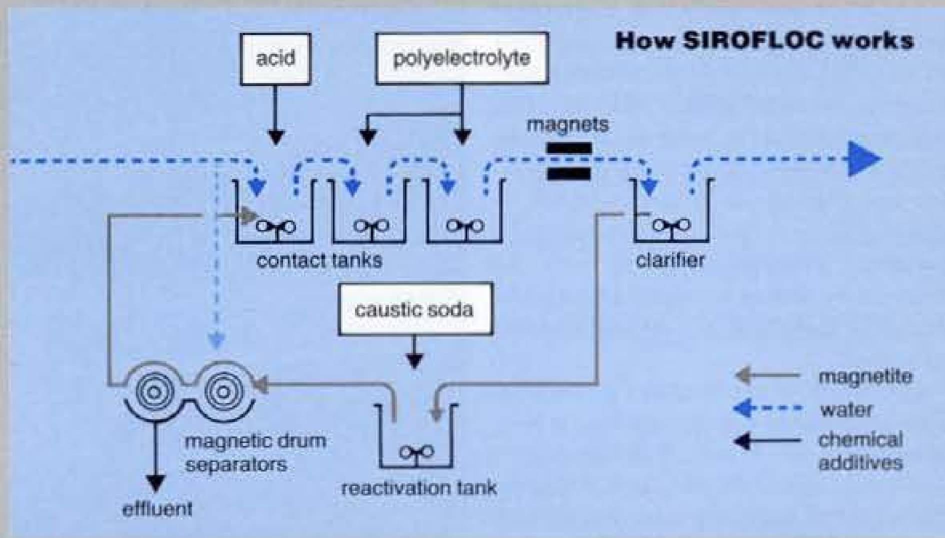
How Sirotherm and SIROFLOC work

The separation principles underlying SIROFLOC and Sirotherm may be similar, but the techniques involved are very different. In the Sirotherm process, raw water flows into the base of an adsorption column that is divided into a number of 'cells', each containing magnetic resin beads, and rises through a rain of circulating resin.

The cleaned water flows out at the top, while the loaded resin is pumped to a regeneration column. There it is stripped with hot water, rinsed (using clean water from the adsorption column), and pumped to the top of the adsorption column. The concentrated effluent is removed for evaporation or disposal.

Magnetic resin systems employing chemical regenerants — for example, the recovery of heavy metals such as nickel from plating rinse water — use a similar method. The loaded resin from the bottom of the absorption column is pumped to the regeneration column, where it is stripped with sulfuric acid, rinsed, and reactivated with alkali before being transferred to the top of the regeneration column. The regeneration effluent is a nickel-rich stream that is used to 'top up' the plating bath.

The SIROFLOC system, on the other hand, uses the same basic techniques for drinking-water clarification, sewage treatment, and the extraction of metals from industrial waste-water. Raw water flows into a series of contact tanks, into which is pumped a 1–3% slurry of magnetite particles. In the first tank the raw water is agitated mechanically and sulfuric acid is added to induce a positive charge on the surface of the magnetite, enhancing the attraction of negatively charged pollutants. Adsorption takes place in the second and third tanks, assisted by a polyelectrolyte.



SIROFLOC uses magnetite to strip pollutants from drinking water, sewage, or industrial waste-water: the magnetite is regenerated and recycled.

From the contact tanks the water containing the loaded magnetite passes between the poles of a permanent magnet; the magnet encourages the magnetite particles to clump together, forming a dense sludge that settles rapidly in a clarifying tank.

The settled magnetite is then regenerated and recycled for re-use. First, sodium hydroxide is added to the loaded magnetite, causing the surface of the particles to become negatively charged and repelling the adsorbed pollutant. Next, the magnetite passes over two magnetic drum separators — large stainless steel drums that rotate around a fixed magnet. The magnetite particles align themselves to the magnet, further shedding any attached pollutant, and are washed free.

The clean magnetite is collected and recycled: laboratory and commercial trials indicate that it has a virtually unlimited 'working life', and so little escapes the treatment system that magnetite replacement is a negligible element in running costs. The water, now cleaned of colour, sewage, or metals, is pumped to further units for disinfection and acidity balance (in the case of drinking water) or for disposal. The concentrated sludge is removed for anaerobic digestion (in the case of sewage) or for disposal in evaporation ponds (in the case of drinking water and industrial effluent). Water used in disposal is returned to the system inlet.

Disposing of effluent sludges from waste-water treatment plants has become a major problem in urban areas. No longer can sludge merely be put to use in agriculture or disposed of for landfill: the heavy metals it contains can lead to major health and environmental problems.

Incineration carries the disadvantages of air pollution, heat production, and especially cost (it is almost three times as expensive per tonne as agricultural disposal and twice as costly as dumping for landfill).

The challenge has been to devise a method of stripping heavy metals from sludge as cheaply as possible. In collaboration with AUSTEP (the Melbourne licensee of the SIROFLOC process), Mr Bob Swinton and Mr Norman Becker carried out laboratory and pilot-scale experiments at a waste-water treatment plant, using magnetic resin beads of varying sizes and the same off-the-shelf magnetic drum separators that SIROFLOC employs.

They have found useful removal of heavy metals and only 5 mL 'leakage' of resin per thousand litres of sludge treated — well within the economic limits established for the process. In a full-scale commercial operation, a scavenging magnet downstream of the treatment area would recover this overflow: the treated sludge can then be spread on land as a safe soil conditioner and low-grade fertiliser.

Carson Creagh

More about the topic:

Extraction of heavy metals from sludges and muds by magnetic ion-exchange. E.A. Swinton, R.J. Eldridge, N.S.C. Becker, and A.D. Smith. *Proceedings of the Sewage Sludge Treatment and Use Symposium, Amsterdam 1988.*

An alternative way to treat sewage. A.J. Priestley, D.L. Sudarmana, and M.A. Woods. *Proceedings of Chemeca '88 Conference, Sydney 1988.*

Purification of pressure leach liquor for zinc electrowinning: a comparison of the hematite and magnetite processes for iron removal. M.E. Cassar, D.R. Dixon, and G.J. Sparrow. *Proceedings of the Non-ferrous Smelting Symposium, Port Pirie 1989.*

The SIROFLOC process: development, construction and operating experience of a 20 000 m^3/day potable water plant. R.J. Maloney, G.P. Home, and M. Stockley. *Proceedings of the Institution of Chemical Engineers Symposium, 1989.*