Bacterial Reduction of Hexavalent Chromium: A Viable Environmental Solution to the Treatment of Effluent from a Ferrochrome Smelter

Willem A Gericke
Billiton Centre for Pyrometallurgy
PO Box 658, Krugersdorp
1740 South Africa

1. ABSTRACT

The project was initiated with the objective of providing a cost-effective, industrially robust, and environmentally sound process for the treatment of hexavalent chromium effluent originating from the production of ferrochrome.

At first, laboratory-scale work under aerobic conditions was undertaken on bacteria imported from the USA. The system was optimised for variables including pH, temperature, nutrient type (e.g. glucose, molasses) and nutrient addition rate. As the effluent could contain phenols, tolerance to phenols at different concentrations was also investigated, including the possibility of utilising phenol as a source of nutrient. Bacteria were subjected to varying concentrations of Cr^{6+} and the rate of Cr^{6+} reduction was monitored. It was found that the Cr^{6+}-reducing ability of the original imported bacteria was inhibited by naturally occurring bacteria found in the industrial effluent.

These bacteria were thus isolated and cultivated under both aerobic and anaerobic conditions in the laboratory. The aerobic bacteria showed the most promise in terms of their ability to reduce Cr^{6+} to Cr^{3+}. DNA homology indicated that the bacteria thus isolated were a new species. A similar optimisation programme was again followed in order to determine optimal conditions for the reduction of Cr^{6+}-containing effluent.

The next phase of the project involved the setting up of an industrial-scale sewage treatment plant to treat the Cr^{6+}-containing plant effluent as a by-pass stream from a slimes dam. Extensive instrumentation and control systems were installed, but it was found that the plant could operate successfully with little supervision in a batch mode. Nutrient type and addition rates were optimised.

It was demonstrated that bacterial reduction of Cr^{6+} was a viable and cost effective method of addressing an environmental problem whereby Cr^{6+}-levels in the effluent were reduced to within the legal limits. The new species of bacteria and their application have been patented.

2. INTRODUCTION

The production of ferrochrome in an electric submerged arc furnace is associated with the co-production of waste products such as slag, bag filter dust and scrubber sludge, which create environmental problems if not managed properly.[1,2] In particular, bag filter dust from an electric furnace or scrubber sludge from an oxidising process such as an oxygen blown converter may contain appreciable quantities of hexavalent chromium. Environmental legislation in most countries prevents the uncontrolled dumping of such wastes, due to the toxic and carcinogenic nature of the dust or sludge.

Conventional treatment and remediation of such wastes include landfilling in approved and controlled landfills, recycling, solidification and stabilisation, etc. However, prior to any of the above-mentioned processes, it is necessary to reduce the Cr^{6+} content of the waste to within the applicable legal limits. Reducing agents commonly used include Fe^{2+} such as $FeCl_2$ or $FeSO_4$ and S^{4+}. Disadvantages associated with the use of such materials are i.e. the high treatment costs, secondary environmental problems such as excessive chlorides or sulphates released into the environment and problems with controlling and optimising the process.

At Samancor Chrome, a major producer of all commercial grades of ferrochrome, reduction of Cr^{6+} to the largely insoluble, non-toxic Cr^{3+} was effected by means of $FeSO_4$ additions in excess of stoichiometric requirements to the slurried dust and sludge. This process was costly and in certain cases the final effluent had to be treated with lime to increase the pH to ≥ 9 in order to ensure that the Cr^{3+} precipitated as insoluble $Cr(OH)_3$.

A review of published literature indicated that bacterial reduction of hexavalent chromium could be a viable alternative to chemical reduction.[3] Thus, a systematic program was developed to evaluate the technical feasibility and economic viability of this alternative compared to conventional treatment of Cr^{6+}-containing wastes. A prerequisite for the process was the ability to operate with minimal supervision and that the effluent from such a plant should meet the environmental standards. It should furthermore equal or better the Fe^{2+} reduction treatment costs.

3. LABORATORY INVESTIGATION

Following on from a literature review, two aerobic Cr^{6+} reducing bacteria were obtained from the Idaho National Engineering Laboratory (INEL), viz. *Pseudomonas aeruginosa* (PA 01) and *Pseudomonas fluorescens* (LB 300). According to published literature,[4] the bacteria were streaked onto Vogel Bonner (VB) agar containing 0.25, 50 and 100 ppm Cr^{6+} as K_2CrO_4. This was done to ascertain that the bacteria were viable, resistant to chromium and uncontaminated. The standard diphenyl carbaside method was used for the determination of Cr^{6+} as an indication of the ability of the bacteria to reduce Cr^{6+}

The first experiment involved inoculating the bacteria into a liquid VB medium containing 50 and 100 ppm Cr^{6+}. The experiment was run for 8 days.

Similar experiments were conducted at 20 and 50 ppm Cr^{6+} to determine the respective rates of reduction. Further experiments were conducted to determine the effect of pH on the Cr^{6+} reducing ability of the bacteria. The use of phenol present in industrial effluents as a nutrient was also investigated.

The results[5] indicated that:

- Bacteria were able to reduce Cr^{6+} at concentrations of up to 50 ppm whilst at a concentration of 100 ppm, Cr^{6+} was toxic to the bacteria. See Table 1 for results.
- Rate of reduction decreased with an increase in Cr^{6+} concentration.
- At a pH of < 6.0, no chrome reduction took place.
- Bacteria were able to utilise phenol as an energy source. Phenol could however not act as an electron donor.

Bacteria	Initial Cr^{6+} concentration (ppm)	Cr^{6+} concentration after 6 days (ppm)	Cr^{6+} concentration after 8 days (ppm)
P aeruginosa	50	5	< 2
P aeruginosa	100	100	100
P fluorescens	50	< 1	<< 1
P fluorescens	100	80	80

Table 1: Effect of Cr^{6+} concentration on the reduction of Cr^{6+} by bacteria

A further experiment involved utilising Cr^{6+} containing industrial effluent from one of the plants as a source of chromium to determine the efficiency of chromium reduction. It was found that the indigenous bacteria present in the effluent inhibited the efficiency of chromium reduction of the bacteria obtained from INEL. It was thus concluded that the use of *P aeruginosa and P fluorescens* to reduce chromium in the effluent would not be successful, as the indigenous bacteria would eventually replace the pseudomonas. The focus of the investigation thus shifted towards isolating, identifying and optimising the efficiency of the indigenous bacteria with respect to reduction of hexavalent chromium.

4. INDIGENOUS BACTERIA

Hexavalent chromium containing effluent samples were collected from various sources at the different plants. These were introduced into nutrient media specifically designed to enhance aerobic and anaerobic growth of as wide a range of bacteria as possible. The aerobic nutrient medium was VB broth utilising glucose as energy source, whilst the anaerobic medium was KSC broth which has acetate as energy source.

Both media contained 25 ppm Cr^{6+} as K_2CrO_4. The addition of the chromate gave a bright yellow colour to the medium. This colour disappeared when the Cr^{6+} was reduced to Cr^{3+}.

An activated sludge reactor with a 4 ℓ working volume was constructed in the laboratory. A peristaltic pump supplied the nutrient, glucose. The reactor was aerated and the pH controlled between 6.6 and 6.8. A return settler was connected to the sludge reactor via a peristaltic pump which returned the sludge to the reactor whilst the supernatant clear liquid flowed into a waste receiver. The system was started with activated sludge from a local sewage works. The bacteria were added to the activated sludge in the reactor. The flow rate was adjusted to give a turnover of 20 hours. The temperature was thermostatically controlled at 25 °C.

Plant effluent containing 13 – 15 ppm Cr^{6+} was added to the reactor, replacing 25% of the tap water, then 50% and finally 100%. Within 22 hours, the Cr^{6+} levels had dropped to 2 ppm.

An aerobic bacterium, which exhibited a strong potential for Cr^{6+} reduction was isolated. This bacterium was characterised at the Microbiology Department of the University of Cape Town as an Enteric, possibly *Enterobacter cloacae*, using the API 20E system. Subsequently the bacterium was further characterised by 16S rDNA sequencing. The sequencing indicated that although the bacterium was an Enteric, little DNA homology existed with any of the bacteria in this group. *Enterobacter cloacae* has been described in literature as being able to reduce Cr^{6+} under anaerobic conditions. The bacteria thus isolated do not do this. The bacterium may thus be a new Enteric, aerobic, Gram-negative, rod-shaped bacterium. An isolate of the bacterium was subsequently deposited at the American Type Culture Collection (ATCC) in Manassas, Virginia.

Further experiments at higher concentrations of hexavalent chromium in the feed to the activated sludge reactor gave results as shown in Table 2.[6] The pH was maintained between 6.6 and 6.8 with an influent rate equal to a turnover of the contents of the reactor of 20 hours.

Initial concentration (ppm Cr^{6+})	Final concentration (ppm Cr^{6+})
25	1
35	2
66	3.5

Table 2: Reduction of Cr^{6+} by *Enterobacter cloacae*

5. PILOT PLANT

The experimental results obtained under laboratory conditions were so encouraging, that a decision was taken to prove the concept at pilot plant scale. The Ferrometals plant of Samancor Chrome in Witbank in the province of Mpumalanga, South Africa, was chosen as the location for the pilot plant. Ferrometals produces charge chrome (ChCr) in closed and semi-closed furnaces as well as medium carbon ferrochrome (MCFeCr) from liquid ChCr in an oxygen blown CLU converter.

Bag filter dust from the semi-closed furnaces is either micropelletised and recycled to the furnaces or slurried and pumped to a slimes dam. Sludge from the gas cleaning system of the closed furnaces and converter is also pumped to the slimes dam. The sludge is allowed to settle and the clear water from the slimes dam is returned to the gas scrubbers. It was decided to treat a bleed stream from the return water line of the slimes dam to the gas cleaning plants.

A small industrial sewage plant with a capacity of 25 m^3, together with the necessary infrastructure was installed as a pilot plant. Figure 1 illustrates the flow diagram of the pilot plant. A blower provided aeration and the pH was controlled by means of sulphuric acid additions via a pH controller. Nutrients were provided from a 1 m^3 tank. Nutrients consisted of molasses, a by-product of the sugar cane industry, nitrogen and phosphorus. Initially, nutrient additions were controlled by a rotameter calibrated at regular intervals.

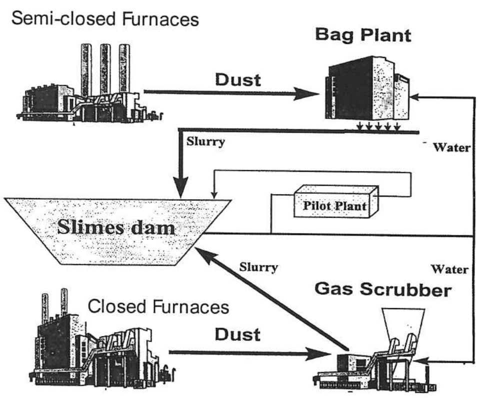

Figure 1: Flow Diagram of Pilot Plant

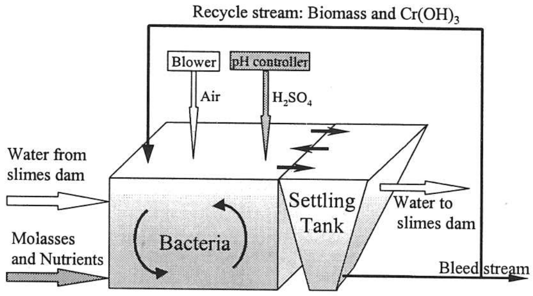

Figure 2: Schematic representation of the pilot plant

As it was envisaged to operate the plant on a continuous basis for at least three months during autumn and part of winter, provision was made for temperature control by the installation of eight 3 kW electric heaters. Temperatures during the night could easily drop to as low as 0 to 5°C from a daytime average of 20 – 25°C. Thus as a further precaution, the plant was thermally insulated by cladding the reactor with sheets of 25 mm thick polystyrene. Figure 2 is a schematic representation of the pilot plant.

The operation of the plant was relatively simple. The influent into the plant was taken from a bleed stream from the return line of the slimes dam. The flow rate was controlled by means of a rotameter. Sludge from the local sewage works was used to start the system. The suspended solids consisting of the bacteria/biomass overflowed from the air agitated compartment into the settling tank where the suspended solids settled under gravity. Any scum and flotsam flowed back into the aerated compartment over an overflow weir. Clarified water flowed over the weir plates and was pumped back to the slimes dam. Solids were continuously pumped back into the aeration compartment via a return sludge line using an air-lift mechanism. The blower also pumped air through the return line. As the aerated pulp has a lower density than the pulp in the settling compartment, the pressure differential resulted in a flow. Solids, consisting mainly of $Cr(OH)_3$ were discharged intermittently from the settling compartment to the slimes dam.

6. PILOT PLANT OPTIMISATION

In order to optimise the operation of the pilot plant, further experiments were conducted in the 4 ℓ laboratory reactor. The objectives and results[7] of these experiments were as follows:

- Determine the most cost efficient, minimum nutrient requirements.
  - The glucose was replaced by molasses. The molasses acted as both energy source and electron donor. The molasses addition was systematically reduced. Nitrogen and phosphorus were added as K_2HPO_4 and $(NH_4)_2SO_4$ respectively.
- Determine the pH tolerance of the bacteria.
  - Bacterial growth was restricted to a pH range of between 4 and 9.
- Determine the optimum pH range for bacterial reduction of Cr^{6+}.
  - Optimal reduction of hexavalent chromium occurred in the pH range of between 6 and 8.
- Determine the bacterial tolerance towards Cr^{6+}.
  - The bacteria were exposed to aqueous concentrations of Cr^{6+} up to 1 000 ppm. It was found that Cr^{6+} concentrations above 500 ppm were toxic to the bacteria. This indicated the resistance of *Enterobacter cloacae* towards hexavalent chromium.
- Determine the growth rate of the bacteria.
  - At 30°C the time taken to double the number of bacteria per mℓ was 1.1 hours whilst at 25°C the doubling time was 1.3 hours.

7. PILOT PLANT OPERATION

A staged inoculation process was followed to introduce the bacteria into the pilot plant. The first stage involved preparing a 25 ℓ volume of bacteria in the laboratory. The nutrients were molasses, K_2HPO_4 and $(NH_4)_2SO_4$.

During the second stage which lasted six days, the contents of the 25 ℓ container were transferred to a 200 ℓ tank, using the same nutrient addition. This tank was aerated and contained 50 ppm Cr^{6+} as potassium dichromate.

For the next stage which lasted seven days, the volume was increased to 1 000 ℓ with effluent from the sludge dam. The initial hexavalent chromium content was 10 ppm. The pH was controlled at 6.5.

The next stage involved transferring the 1 000 ℓ inoculant to the pilot plant and filling the pilot plant to 10 000 ℓ. Nutrient addition was maintained as before and the blower provided aeration.

At the final stage, the plant was filled to capacity (25 000 ℓ) with effluent. Temperature was controlled between 20 °C and 30 °C. The pH was controlled at 6.5 ± 0.5. The initial flow rate was 500 ℓ/h. After 30 days this was increased to 1 000 ℓ/h and maintained at that rate. The plant was operated for a further 25 days at a flow rate of 1 000 ℓ/h. Thereafter, the flow rate was increased for a further 40 days to 1 500 ℓ/h without increasing the addition of molasses, K_2HPO_4 or $(NH_4)_2SO_4$. During the final phase of continuous operation lasting 5 days, the flow rate was increased to 2 000 ℓ/h, again without a corresponding increase in the nutrient addition rate. The Cr^{6+} concentration and the bacterial count were measured regularly.

Occasional infestations of protozoa occurred during the initial stages of growing up the bacteria. However, these were effectively controlled by raising the pH to 11 for 1 hour before dropping it again to 6.6, thus killing the protozoa whilst the bacteria survived.

Modifications were made to the sludge handling system at Ferrometals during the installation and commissioning of the pilot plant. These involved rerouting the sludge and dust slurry from the furnaces and converter to a new effluent treatment plant, thus isolating the original sludge dam from the rest of the plant. This implied that the sludge dam received no influent from the furnace and converter gas cleaning plants, thereby creating an ideal environment to determine the viability of bacterial reduction of Cr^{6+}.

The plant was operated continuously for a period of 100 days.[8] During the latter phases nutrient additions were made daily in batches, instead of continuously. This was done in an attempt to determine how robust the bacterial reduction process would be as well as to simplify the operation of the plant. It was shown that intermittent as opposed to continuous addition of nutrients had no detrimental effect on the efficiency of bacterial reduction. This was proven by regular bacterial counts and by regular analysis of the Cr^{6+} levels in the influent into and effluent from the pilot plant. Operating results as given by Cr^{6+} analyses in the influent and effluent are given below. The use of the novel *Enterobacter cloacae* under aerobic conditions to reduce hexavalent chromium in industrial effluent was patented.[9]

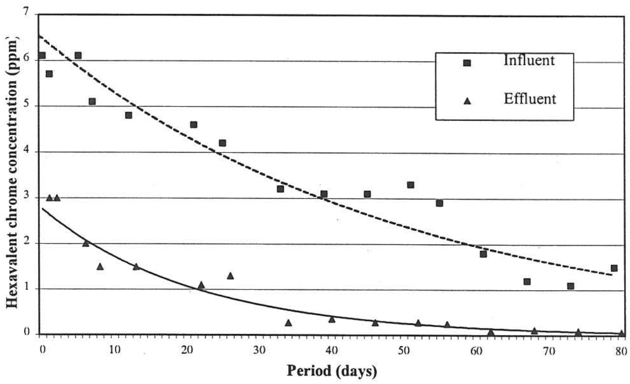

Figure 3: Cr^{6+} levels in the influent and effluent of the pilot plant

8. CONCLUSIONS

It was proven conclusively that the new strain of bacterium, identified as *Enterobacter cloacae* isolated in the industrial effluent, has the ability to reduce Cr^{6+} at concentrations up to 50 ppm. The bacteria were able to survive under laboratory conditions at a concentration of 500 ppm. The optimum pH range for efficient bacterial reduction was found to be 6.0-8.0. Bacterial growth was inhibited below 20°C and above 30°C. Glucose as a source of energy and as an electron donor was successfully replaced by the cheaper molasses. Periodic infestations of protozoa were successfully controlled by raising the pH to 11 for a period of 1 hour before reducing it to within the operating pH range. Nutrient additions were optimised and further optimisation is possible, thereby reducing operating costs even further. As a result of changes to the effluent treatment system at Ferrometals, it was possible to operate the pilot plant in isolation from the rest of the plant in closed circuit with the slimes dam. Continuous operation of the pilot plant over a period of 100 days resulted in a reduction in Cr^{6+} levels of the slimes dam to 0.07 ppm at the end of the period. This is very close to the South African legal limit of 0.05 ppm. The bacterial reduction process proved to be robust inasmuch as the plant operated efficiently even when nutrient additions were made intermittently on a daily basis instead of continuously.

9. ACKNOWLEDGEMENTS

The author wishes to thank Samancor Chrome and Billiton Process Research for permission to publish the paper. The author is indebted to his many colleagues who contributed to the operation of the laboratory reactor and the pilot plant. In this regard, I would like to mention Dr. Ellen Lawson, Ms Susan Lenes, Messrs Trevor Tunley, Paul Barnard and Clint Bowker.

10. REFERENCES

1. Gericke, WA. *Environmental Aspects of Ferrochrome Production,* INFACON7, Trondheim, (1995), 131-140.
2. Gericke WA. *Environmental solutions to Waste Products from Ferrochrome Production*, INFACON8, Beijing, (1998) 51-58.
3. Andersson, K, Rosèn, M. *Biological Reduction of Hexavalent Chromium in a Leachate from Värgon Alloys AB,* VATTEN.3.97, (1997), 245-251.
4. Bopp, LH, Chakrabarty, AM, Ehrlich, HL. *Chromate Resistance Plasmid in Pseudomonas fluorescens.* Journal of Bacteriology 155, (1983), 1105-1109.
5. Lawson, EN. *Bacterial Reduction of Chrome (vi) to Chrome (iii).* Gencor Process Research Report PR 95/08. Unpublished.
6. Lawson EN. *Bacterial Reduction of Hexavalent Chrome Phase 2*, Gencor Process Research Report PR 97/47 (1997). Unpublished.
7. Lawson EN. *Bacterial Reduction of Hexavalent Chromium: Phase 3*, Gencor Process Research Report PR 99/09 (1999). Unpublished.
8. Tunley TH, Barnard, P. *Bacterial Reduction of Hexavalent Chromium: Pilot Plant Operation at Ferrometals.* Billiton Process Research Report PR 99/32 (1999). Unpublished
9. Gericke WA, Lawson EN. *South African Patent 99/0184*, (filed 03.12.1999).