

TRACE ELEMENT REMOVAL TECHNIQUES WITH IRON OXYHYDROXIDES AND THE ADSORPTION/CO-PRECIPITATION REMOVAL MECHANISM

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DECLARATION

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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*Note all attachments provided on CD as electronic copies

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ABSTRACT

The environmental impact of trace elements, in particular selenium in the selenite form, from discharge of ash dam water from Vales Point Power Station into Wyee Bay on Lake Macquarie New South Wales Australia is of concern, and has been the subject of a number of scientific investigations. These include both control of discharge and studies of effects on aquatic flora and fauna including the biomagnification or bioaccumulation and biotransference of selenium in fish and benthic organisms. Cost-effective and efficient chemical control of trace elements discharged to the environment is at the core of this study.

Measures to control the quantity and quality of ash water discharges from Vales Point Power Station has been proactively managed by the electricity generation industry over the past decade in the form of plant modifications and reduction in catchment inflows. Studies have been undertaken looking at a range of treatment options inclusive of precipitation (coagulation/flocculation), bioreactors and oxidised metallic iron. The latter treatment and sole focus of this thesis has been found to be potentially the most viable treatment option owing to its high efficiency of removal of selenium and other trace elements including arsenic, vanadium, antimony, chromium and to a lesser extent aluminium and molybdenum. Metallic iron was found to be the most viable treatment option owing to its availability, low cost and minimum operating and maintenance requirements.

Pilot plant investigations undertaken at Vales Point Power Station from 2002 to 2008 exploring the use of a number of iron products including iron bars, steel plates and steel wool revealed that the iron oxides and oxyhydroxides formed on the surface of metallic iron and responsible for the core processes of adsorption and coprecipitation of selenium and targeted trace elements were goethite, lepidocrocite, hematite and magnetite. Characterisation of these iron oxides and oxyhydroxides formed by the pilot plant employed X-Ray Diffraction and Scanning Electron Microscope Imagery, involving comparisons with synthetic samples.

The efficiency of selenium and trace element removal was found to be influenced by a number of parameters inclusive of surface area of metallic iron, crystal structure and surface area of iron oxides and oxyhydroxides formed on the iron surface, pH, solution matrix and concentration of targeted trace elements in ash water. Pilot plant test results with loosely packed steel wool over a six month period yielded the highest efficiency of removal owing to its high surface area with selenium reduced by 85% (on average), arsenic by 87%, antimony by 87%, chromium by 80%, vanadium by 97%, aluminium by 21% and molybdenum by 48%.

Adsorbed ions are generally not leached under natural environmental conditions over extended periods of time. Leachate studies of oxidised material from pilot plant operations were performed during 2003-2004. Samples stored with ash water over extended periods exhibited very little redissolution in the case of selenium, arsenic, antimony and aluminium with some test results indicating only 1% redissolution back into solution. Molybdenum was the only trace element that did display limited leaching with final levels being two to three times that in the initial ash water. Further studies in 2007 and 2008 by the USEPA Method 1311 leaching procedure provided no detectable levels of selenium, arsenic, antimony, chromium, vanadium and molybdenum. The only element which had modest levels above the detection limit was aluminium.

The surface area measured for synthetic/commercial samples of iron oxides and oxyhydroxides of goethite, hematite, lepidocrocite and magnetite differed, and influenced removal efficiency. Test results of laboratory trials with solution matrices of demineralised water, sodium sulphate solution, sodium chloride solution and ash water yielded overall efficiency of removal of selenite with each oxide in the following order: lepidocrocite > goethite > hematite > magnetite.

During laboratory trials at pH 8 and above, all systems displayed the following efficiency of removal of selenite in terms of the matrix of the solution: ash water > sodium chloride solution > sodium sulphate solution > demineralised water. This is an important aspect as the pH of Vales Point Power Station ash water fluctuated between 7.5 and 8.5 in the pilot plant trials, whereby high efficiency of trace element removal was achievable.

The rate profiles during laboratory trials for selenium, arsenic, chromium, vanadium, antimony, aluminium and molybdenum revealed that, overall, these trace elements were very rapidly adsorbed with the observed half-life of the initial process being in the order of one to two minutes. This rapid uptake highlights the benefits of this process, which can successfully deal with large flowing volumes for extended periods without reaching uptake capacity.

Overall, this research has exposed mechanistic aspects of the chemistry involved in iron-based trace element removal, and highlighted the beneficial nature of the process as being a highly efficient low-cost option for the treatment of process water (ash water) in high salinity or estuarine waters for the removal of trace elements of concern to the receiving environment such as selenium and arsenic.

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GLOSSARY OF ABBREVIATIONS AND TERMS

Å	Angstroms
AF	Affectation Factor
AIP	Aqueous-ion activity product
ALS	Australian Laboratory Services
ANZECC	Australian and New Zealand Environment Conservation Council
BC	Brine Concentrator
BET	Brunauer-Emmett-Teller method
ccp	Cubic close packing
CSIRO	Commonwealth Scientific Industrial Research Organisation
DFT	Density functional theory
DL	Detection Limit
DLM	Double Layer Model
ECL	Environmental Concern Level
EGME	Ethylene Glycol Monoethylether Technique
EPRI	Electric Power Research Institute of the United States of America
EXAFS	X-ray Absorption Fine Structure
hcp	Hexagonal close packing
HDPE	High Density Polyethylene
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectroscopy
iep	Ion Exchange Potential
LC50	Lowest concentration of a toxicant that kills all the test organisms
m²/g	Meter Square per Gram
mg/kg	Milligrams Per Kilogram
mg/L	Milligrams Per Litre
µg/L	Micrograms Per Litre
NZVI	Nano Zero-Valent Iron
NHMRC	National Health and Medical Research Council
NIPDWS	National Interim Primary Drinking Water Standards
ORC-ICPMS	Octopole Reactive Cell Inductively Coupled Plasma Mass Spectrometer
pcz	Point of Zero Charge
ppm	Parts Per Million
PQL	Practical Quantitation Limit
RO	Reverse Osmosis
SEM	Scanning Electron Microscopy
SeO₃²⁻	Selenite
SeO₄²⁻	Selenate
SRB	Sulfate reducing bacteria
TEM	Transmission Electron Microscopy
TCLP	Toxicity Character Leaching Procedure
TLM	Triple Layer Model
Trigger Values	These are the concentrations (or loads) of the key performance indicators measured for the ecosystem, below which there exists a low risk that adverse biological (ecological) effects will occur.
XRD	X-Ray Diffraction

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