ARCADIS

End of Pipe Metals Removal Technologies Review

Huntsman PU Wilton

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Introduction

Context

Recent testing requested by the Environment Agency (EA) associated with the Hunstman Wilton site's environmental operating permit has highlighted elevated (above laboratory method detection limits) concentrations of metals, Nickel (Ni) and Chromium (Cr) in particular, in the site's effluent discharge. These have been measured in effluent discharged into the permitted outfall location, S1 drain.

It is understood the metals are currently not consented to be discharged under the existing permit, and that S1 drain ultimately discharges into the River Tees via a network of off-site drainage.

Huntsman's preference at this time is to pursue a derogation with the EA, and to support this it is anticipated a review of the potential end of pipe treatment technologies which could be adopted will be required.

Objective

To present an initial high level screening opinion of the potential technical solutions which could be adopted to reduce or eliminate the Ni and/or Cr loading.

Approach

A literature review of techniques available for heavy metals removal from aqueous waste streams was carried out assessing their reported efficiency for nickel and/or chromium removal where available.

A number of methods were shortlisted according to their likely efficiency and internal past experience was used to compare them to each other from a cost and implementation view points.

Heavy Metals in Wastewater - Treatment Methods

Preliminary Assessment for Nickel and Chromium Removal

Method	Method specifics	Drawback	Expected efficiency
Physical separation	Mechanical screening, gravity concentration, magnetic separation, electrostatic separation, attrition scrubbing	Not suitable for dissolved metals	nil
Chemical precipitation	Hydroxide (sodium hydroxide)	Small particle size: filtration issue. Different optimum pH for nickel and chromium hydroxides formation (respectively 6 and 8) Pre-treatment required to reduce Cr(VI) to Cr(III) using sodium metabisulphite at pH 2.5	nil (due to low concentration)
	Sulphide (sodium sulphide, sodium hydrosulphide)	Low concentration: filtration issue. Pre-treatment required to reduce Cr(VI) to Cr(III) using sodium metabisulphite at pH 2.5, followed by neutralisation. Risk of H_2S emission at low pH	minimal

Method	Method specifics	Drawback	Expected efficiency
Chemical precipitation and coagulant addition	Sulphide precipitation followed by addition of coagulant (aluminium sulphate, ferric sulphate, ferric chloride or polymers)	Pre-treatment required to reduce Cr(VI) to Cr(III) using sodium metabisulphite at pH 2.5 followed by neutralisation. Risk of H_2S emission at low pH Production of solid hazardous waste	High for nickel, moderate to high for chromium (better results with polymer coagulant than inorganic)
Chemical precipitation and nanofiltration	Sulphide precipitation and filtration followed by filtration through nanotubes	Costly, designed to remove all ions for water re-use Novel technology	Unknown – outcome is system dependant
Chemical precipitation and ion exchange	Choice of ion exchange dependant on overall composition	Only relevant for high metal ions starting concentrations	n/a

Method	Method specifics	Drawback	Expected efficiency
Chelating precipitation	TMT (trimercaptotriazine), STC (potassium/sodiumthiocarbonate), SDTC (sodium dimethyldithiocarbamate)	Not efficient below 50ppm	nil
	Dithiocarbamate (Metalsorb trade mark)	Excess reagent required to treat ppb level (activated carbon filtration prior discharge necessary to remove excess)	Moderate for nickel, unknown for chromium
	Dipropyl dithiophosphate	Lowest concentration reached 50ppb	nil

Method	Method specifics	Drawback	Expected efficiency
Coagulation	Common inorganic coagulants: Ferric sulfate, aluminum sulfate, ferric chloride. Organic coagulants: Polyamines Polytannate Poly DADMAC (diallyl dimethyl ammonium chloride).	pH and temperature sensitive Used for negatively charged colloids	Nil to low
	SUEZ - Metclear trademark coagulants	Consultation with supplier necessary to obtain relevant information and to design suitable solution Potentially costly	Reported high for nickel by supplier unknown for chromium
	PEX (sodium xanthogenate grafted to polyethyleneimine)	Low pH requirement (3) Novel (experimental)	High at ppm level, unknown at ppb level
Flotation	Ion Flotation (SDS and hexadecyltrimethyl ammonium bromide as collectors, ethanol and methyl isobutyl carbinol as frothers)	Limited efficiency at low concentrations	low

Method	Method specifics	Drawback	Expected efficiency
Ion exchange	General Examples: Carboxylic acid functionality (Purolite C105, C106)	Wide variety of resins available – testing required Chemical solution used to regenerate periodically	Highly dependant on background ions present in solution, pH, temperature, initial concentration, flow rates Experimentation required
	DOWEX 2-X4		High for Cr(VI)*
	Macroporous acidic cation exchange (Indion 790)	Acidic condition	nil
	Epoxy-cross-linked poly ethylenimine		High for Cr(III)*
	Chelix-100		High for Cr(III)*
	Lewatit MonoPlus SP 112 (strongly acidic, macroporous cation-exchange resin)		Low for nickel* No results available for chromium

* Results obtained for experimental laboratory solutions may differ significantly for industrial waste solution

Method	Method specifics	Drawback	Expected efficiency
Ion exchange (cont.)	Purolite (S106) epoxy polyamine	Highly specific – testing required to ensure suitability	High for chromium (VI)* Not tested for nickel
	Macroporous polystyrene strong base with quaternary amine functionality (IRA-900)	Highly specific – testing required to ensure suitability	High for chromium(VI)* Not tested for nickel
	Polyarylic matrix containing a quaternary amine (IRA-458, IRA958, IRA 67)	Highly specific – testing required to ensure suitability	No results available for chromium and nickel
	IRN77 (Resin designed for treatment of cooling water in nuclear plant)	Possible displacement of Ni(II) by Cr(III)	High under correct conditions*
	Natural zeolites Modified zeolite (Clinoptilolite loaded with amorphous iron oxide)	Novel (experimental stage)	Not tested for nickel and chromium at ppb level

* Results obtained for experimental laboratory solutions may differ significantly for industrial waste solution

Method	Method specifics	Drawback	Expected efficiency
Membrane filtration	Utrafiltration	Suitable for macroparticles Concentrates pollutant down creating a second stream requiring treatment/disposal	nil
	Reverse osmosis	Energy demanding, costly Multistage required Suitable only in absence of organic compound and silica, at low alkalinity and hardness.	Potentially high
	Nanofiltration	Costly, highly dependant of ions present in solution, produces a second highly contaminated stream requiring disposal/treatment Wide variety of membrane available, limited testing results for multi-ions solution.	moderate
	Electrodialysis	Costly, highly specialised, demanding maintenance, produces a second highly contaminated stream requiring disposal/treatment	Low for low level nickel and chromium

Method	Method specifics	Drawback	Expected efficiency
Adsorption on multi-walled carbon nanotube	Contact with non-functionalized MWCNs	Adsorption hindered by the presence of chloride or sulphate ions Different optimum pH for chromium and nickel (respectively 3 and 6) Costly Novel technology	high for nickel, moderate to high for chromium depending on pH
Absorption on polymer media	“sponge filters” MetalZorb (Cleanway USA)	Liaising with manufacturer necessary to obtain more information	Reported High (below 1ppb) by manufacturer
Electrolysis	Electrodeposition	Costly, energy demanding, different voltage requirement for chromium and nickel	Dependant on other ionic species present in solution, pH, temperature
	Electrogoagulation (eg ferric chloride as coagulant), stainless steel electrodes	Costly, requires both chemicals and energy input	Not tested for nickel and chromium at ppb level.

Method	Method specifics	Drawback	Expected efficiency
Biosorption (adsorption using different biological media)	Activated carbon	Not well suited for metal ions substrates Becoming more costly	low
	Activated carbon in combination with alginate gel	Very novel, at development stage Requirement for regeneration every 10 cycles using nitric acid	Untested for Ni and Cr
	Natural clay chemically pre-treated using ammonium cations (tetramethylammonium) and acid	Not suitable for ppb level	nil
	Chitosan (naturally occurring polysaccharide with amino and hydroxyl functional groups)	Structural damages under acidic pH Very novel	Not known

Method	Method specifics	Drawback	Expected efficiency
Biosorption (adsorption using different biological media) (cont.)	Derived from non living biomass (eggshells, bark, crustaceous shells) or from algae	Require chemical pre-treatment and energy demanding heat treatment Development stage	Limited for Cr, not known for Ni
	Agricultural waste (lignin and cellulose) Examples: nut shells, saw dust, pine needles… Chemically and thermally pre-treated	Novel Low pH required (acidic) for chromium and nickel removal	Untested at ppb level – expected low Different media efficiency for nickel and chromium
	Algae (chemically pre-treated and dried)	Development stage	Untested at ppb level- expected low
Biological removal using activated sludge		Slow batch process, large space requirement	Low

Summary Table

Selection of Most Potentially Suited Methods

Method	Cost Comparison	Implementation Time Comparison	Implementation Limitations	Environmental Impact notes
Sulphide precipitation followed by addition of polymer coagulant	Lowest	Moderate (trials required to ascertain efficiency of each stage, filtration set up requirement)	Multi-stage, large footprint for equipment	Addition of multiple chemicals to achieve redox and pH Significant quantity of hazardous sludge generated
Coagulation by SUEZ-Metclear trademark coagulants and filtration		Moderate to long (communication with suppliers and trials)	Supplier located in the USA, large footprint	Moderate quantity of hazardous sludge generated
Ion Exchange		Long (identify suitable resin through suppliers and trials)	Possible pre-treatment required	Hazardous waste from regeneration solutions
Absorption on polymer media (MetalZorb)		Long (communication with supplier(s), trials)	Supplier in the USA	Contaminated polymer disposal
Reverse Osmosis (e.g. polyamide thin-film composite)		Moderate (ascertain efficiency, identify suitable membrane system and supplier)	Potential large foot print. Maintenance of membranes	Small amount of contaminated brine for disposal, energy consuming
Electrolysis		Long (find suitable electrodes, voltage, temperature, pH)		Energy consuming
Adsorption on non-functionalized multi-walled carbon nanotube	Highest	Very long (experimental work to ascertain efficiency, potential difficulties in sourcing material)	Lack of scale up knowledge	Small quantity of loaded carbon nanotube

Closing comments

- None of the method listed is guaranteed to remove both chromium and nickel from the given process waste solution.
- Laboratory trials would be required for all options considered.
- Given the low starting concentration it is possible that a combination of methods would be required to achieved a significant decrease.
- For chemical treatment options it would be advisable to consider those where the required chemicals are already in use on site.
- Technology considered should also be of some familiarity to onsite operating and maintenance personnel in order to avoid full reliance on external suppliers.

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