

LoCAL Deliverable D2.2

Interim Report on Influence of Gas Pressures on Clogging Processes

WP number

WP.2

**Partner
responsible**

University of Oviedo (UOVE)



Universidad de Oviedo



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**Low-Carbon After-Life (LoCAL): sustainable use of flooded coal mine voids
as a thermal energy source - a baseline activity for minimising post-closure
environmental risks**



Table of contents

1	Introduction	3
1.1	LoCAL background	3
1.2	Objectives	4
2	Origin of iron in mine water	6
3	Ochre deposits mechanisms	9
4	Influences of hydro-chemical characteristics of mine water in the iron deposits.....	11
4.1	Influence of air oxidation of ferrous iron in mine water	11
4.2	Influence of Carbon dioxide.....	15
5	Control of ochre clogging in geothermal applications	17
5.1	Physical methods to control ochre accretion	18
5.2	Chemical agents to prevent ochre clogging and scaling	20
6	Experiences of clogging in geothermal open loop systems	23
6.1	Experiences in United Kingdom	25
6.2	Experiences in Spain: Barredo Case	25
7	Lesson learned for clogging prevention.....	31
8	Bibliography	33



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1 Introduction

1.1 LoCAL background

This report forms part of the output from the LoCAL (*Low Carbon AfterLife: Sustainable Use of Flooded Coal Mine Voids as a Thermal Energy Source- a Baseline Activity for Minimising Post-Closure Environmental Risks*) project, funded by the European Commission Research Fund for Coal and Steel, grant number RFCR-CT-2014-00001.

The fundamental objective of LoCAL is to provide a number of technical, economic and management tools, aimed at overcoming barriers to the uptake of mine water in abandoned flooded coal mines as a source for heating and cooling (passively, or via the use of heat pumps). The project is divided into five Work Packages (WP) and a number of Tasks.

WP	Task	UoG	Alkane	NTU	UoO	HUNOSA	GIG	Armada
1	1.1 A new tool for heat transfer modelling in flooded mine workings							
	1.2 Quantifying important mixing processes at the system scale							
	1.3 Demonstration of new tools on a system in development							
2	2.1 Preventative strategies for ochre clogging of subsurface pumps and pipework during open-loop heat-pump exploitation of mine waters							
	2.2 Closed-loop strategies for oxidised, ochre-precipitating mine waters in treatment systems.							
3	3.1 Technical, legal and management STEEP/ cost-benefit analysis of various types of decentralised heat pump system, versus centralised plant room system							
	3.2 Pathways to market							
	3.3 Models for incorporating cooling into a delivery system							
	3.4 Ownership, management and financial models							
	3.5 Toolbox assuring multiplication of the project results							
4	4.1 Pilot implementation at Markham site (UK)							
	4.2 Pilot implementation at pilot site in Asturias (ES)							
	4.3 Pilot implementation at pilot site in Bytom (PL)							
5	5.1 Project management							
	5.2 Reporting							
	5.3 Dissemination							

UoG = University of Glasgow (UK), Alkane = Alkane Energy Ltd. (UK), NTU = Nottingham Trent University (UK), a subcontractor to Alkane; UOVE = University of Oviedo (Spain), GIG = Central Mining Institute (Poland). Black boxes indicate Task Manager, grey indicate Task Participant.



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The LoCAL Project aims at providing bespoke tools for investigating flow and heat transfer in flooded mine workings. New tools for quantifying and modelling heat transfer in networks of flooded mine workings are under development. Another aim of the LoCAL project is to overcome the hydrochemical barriers to effective heat transfer from raw and treated mine waters. Ochre clogging is a well-known phenomenon which affects many mine water heating and cooling systems. The LoCAL project covers technical and engineering issues, and provides economic, legal and management models for efficient energy extraction and distribution of various types of decentralised and centralised heat pump.

Project activities are being undertaken in mining areas of the UK by research organizations in partnership with industrial enterprises (University of Glasgow in partnership with Alkane Energy Ltd.), Spain (University of Oviedo, with HUNOSA as the industrial partner) as well as in Poland (Central Mining Institute, in partnership with Armada Development).

This report aims to update the knowledge on clogging processes in mine water management for Workpackage 2 of LoCAL – “Overcoming the hydrochemical barriers to effective heat transfer from raw and treated mine waters”.

1.2 Objectives

Abandoned and flooded mines provide underground reservoirs of mine water that can be used as a renewable geothermal energy source. Mine water can contain dissolved iron and if this is exposed to oxygen, it can oxidize to form oxyhydroxides which can produce incrustations or clog in the elements of a geothermal installation, reducing its performance. Clogging of pumps, heat exchanger, pipes and other subsurface infrastructures is a challenge in mine water management and is necessary to know the key processes that govern its formation and deposition.

The objective of this Report is to fulfil the requirements of Task 2.1 of LoCAL – “Preventative strategies for ochre clogging of subsurface pumps and pipework during open-loop heat-pump exploitation of mine waters”. This Task is part of Workpackage 2, which objectives are to investigate the hydrochemical changes affecting mine waters that are potentially harmful to the use of these waters in effective thermal exchange processes and to develop strategies for minimisation of the effects of these hydrochemical barriers to heat transfer.



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For this purpose a review of the state of art is carried out on the following issues:

- Origin of iron in mine water
- Mechanisms for what accumulation of ochre from flowing mine water occurs
- Influences of hydro-chemical characteristics, dissolved gases, and other parameters of mine water in the iron deposits
- Technics to control ochre clogging in pipelines, pumps and heat exchanger
- Review of experiences of clogging due to mine water with iron content in geothermal open loop systems, with special attention on experiences in UK, Spain and Poland
- Review of experiences in which reducing agents to prevent ochre clogging and/or scaling formation have been used



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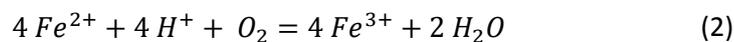
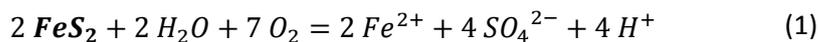


2 Origin of iron in mine water

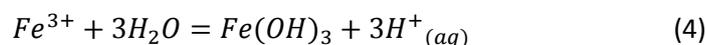
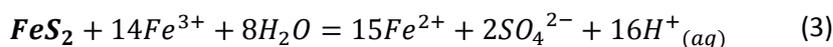
Coal-mine water contains iron and sulfate in solution, and the water is generally acid in the absence of limestone that can buffered the system. Iron sulfides are commonly associated with coal, predominantly in form of pyrite (FeS_2), or the less abundant and stable marcasite, which may form at lower pH and possibly lower sulfur concentration (Ward, 2002). The regeneration of ferric iron (which is reduced to ferrous on reaction with pyrite) is the key reaction in promoting the ongoing oxidation of the mineral. The oxidation of the pyrite (iron disulphide) leads to the production of protons (acidity).

Mining allows the introduction of oxygen to the deep geological environment and thus the oxidation of minerals which previously were in a reduced state. Together with iron minerals, other may play an important role in the acidity of the system. Also, opposite to the generation of acidity, different carbonate minerals present in the coal beds act as acidity consumers. Summary of these is present in the following table extracted from Blodau (2006).

During its oxidation, pyrite undergoes a complex cycle of reactions (Rahman and Bastola, 2014) described with the following set of chemical equations (Singer & Stumm, 1970; Appelo & Postma, 2005):



At pH below 3.5 most of the ions of Fe(III) remain in the solution and are an additional oxidising factor, ferric iron then may act as an electron acceptor for further pyrite oxidation, or hydrolysis may occur, both processes releasing further protons:





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This is the phenome that causes the so-called acid mine drainage (AMD). The acidity generated by such reactions only results in a significantly depressed pH in the mine water when it exceeds the alkalinity available in the system (Jamieson, 2011; Silva et al., 2011). Such alkalinity may be available as bicarbonate in groundwater or in the form of mineral phases (Banks et al., 1997).

Selected processes causing changes in acidity of mine waters

Processes involved in acidity generation

I Redox reactions

Stoichiometry

- | | |
|----------------------------|---|
| (1) Pyrite oxidation | $\text{FeS}_2 + 3.5\text{O}_2 + 3\text{H}_2\text{O} \Rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$ |
| (2) Pyrite oxidation | $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \Rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$ |
| (3) Ferrous iron oxidation | $\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ \Rightarrow \text{Fe}^{3+} + 0.5\text{H}_2\text{O}$ |
| (4) Pyrrhotite oxidation | $\text{FeS} + 2\text{O}_2 \Rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-}$ |
| (5) Sulfur oxidation | $\text{S}(0) + 1.5\text{O}_2 + \text{H}_2\text{O} \Rightarrow 2\text{H}^+ + \text{SO}_4^{2-}$ |
| (6) Chalcopyrite oxidation | $\text{CuFeS}_2 + 4\text{O}_2 \Rightarrow \text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{SO}_4^{2-}$ |
| (7) Sphalerite oxidation | $\text{ZnS} + 2\text{O}_2 \Rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-}$ |

II Heterogeneous reactions — precipitation (secondary)

- | | | |
|---------------------|--|---|
| (8) Ferrihydrate | $\text{Fe}(\text{OH})_3 + 3\text{H}^+ \Leftrightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$ | $\text{p}K_s = -4.81^2$ |
| (9) Jurbanite | $\text{Al}^{3+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \Leftrightarrow \text{AlOHSO}_4 + \text{H}^+$ | $\text{p}K_s = 3.8$ |
| (10) Alunite | $\text{K}^+ + 3\text{Al}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \Leftrightarrow \text{KAl}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$ | $\text{p}K_s = 1.4^2$ |
| (11) K-Jarosite | $\text{K}^+ + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \Leftrightarrow \text{KFe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+$ | $\text{p}K_s = 9.21^2$ |
| (12) H-Jarosite | $3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \Leftrightarrow \text{HFe}_3(\text{SO}_4)_2(\text{OH})_6 + 5\text{H}^+$ | $\text{p}K_s = 5.39^4$ |
| (13) Schwertmannite | $\text{Fe}_8\text{O}_8(\text{OH})_x(\text{SO}_4)_y + (24-2y)\text{H}^+ \Leftrightarrow 8\text{Fe}^{3+} + y\text{SO}_4^{2-} + (24-2y+x)/\text{H}_2\text{O}$ | $\text{p}K_s = -18$
$\pm 2.5^1; 10.5$
$\pm 2.5^3$ |
| (14) Goethite | $\text{FeOOH} + 3\text{H}^+ \Leftrightarrow \text{Fe}^{3+} + 2\text{H}_2\text{O}$ | $\text{p}K_s = -1.4^1$ |
| (15) Melanterite | $\text{Fe}^{2+} + \text{SO}_4^{2-} + 7\text{H}_2\text{O} \Leftrightarrow \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ | $\text{p}K_s = 2.46^6$ |
| (16) Gibbsite | $\text{Al}^{3+} + 3\text{H}_2\text{O} \Leftrightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+$ | $\text{p}K_s = -8.04$ |
| (17) Siderite | $\text{Fe}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O} \Leftrightarrow \text{FeCO}_3 + 2\text{H}^+$ | $\text{p}K_s = -10.45$ |
| (18) Rhodotrosite | $\text{Mn}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O} \Leftrightarrow \text{MnCO}_3 + 2\text{H}^+$ | |
| (19) Gypsum | $\text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \Leftrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ | $\text{p}K_s = 4.58^2$ |

III Mineral transformation

- | | |
|--|---|
| (20) Schwertmannite ⁸ -goethite | $\text{Fe}_8\text{O}_8(\text{OH})_{5.5}(\text{SO}_4)_{1.25}(\text{s}) + 2.5\text{H}_2\text{O} \Leftrightarrow 8\text{FeOOH}(\text{s}) + 2.5\text{H}^+ + 1.25\text{SO}_4^{2-}$ |
|--|---|

Processes involved in consumption of acidity

I Heterogeneous reactions — dissolution

(21) Calcite	$6.4 < \text{pH} < 10.4 : \text{CaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$
(22) Calcite	$\text{pH} < 6.4 : \text{CaCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{CO}_2(\text{g})$
(23) Dolomite	$6.4 < \text{pH} < 10.4 : \text{MgCa}(\text{CO}_3)_2 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-$
(24) Dolomite	$6.4 < \text{pH} < 6.4 : \text{MgCa}(\text{CO}_3)_2 + 4\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$
(25) Biotite	$\text{K}(\text{Mg}, \text{Fe}(\text{II}))_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2(\text{s}) + 7\text{H}^+ \rightleftharpoons \text{K}^+ + 3(\text{Mg}^{2+}, \text{Fe}^{2+}) + \text{Al}(\text{OH})_3(\text{s}) + 3\text{SiO}_2(\text{s}) + 3\text{H}_2\text{O}$
(26) Plagioclase	$\text{Na}_{0.7}\text{Ca}_{0.3}\text{Al}_{1.3}\text{Si}_{2.7}\text{O}_8(\text{s}) + 1.3\text{H}^+ + 1.3\text{H}_2\text{O} \rightleftharpoons 0.3\text{Ca}^{2+} + 0.7\text{Na}^+ + 1.3\text{Al}(\text{OH})_3(\text{s}) + 2.7\text{SiO}_2(\text{s}) + 3\text{H}_2\text{O}$
(27) Orthoclase	$\text{K}(\text{Fe}(\text{II})_{1.5}\text{Mg}_{1.5})\text{AlSi}_3\text{O}_{10}(\text{OH})_2(\text{s}) + 7\text{H}^+ + 3.75\text{H}_2\text{O} + 0.375\text{O}_2(\text{aq}) \rightleftharpoons \text{K}^+ + 1.5\text{Mg}^{2+} + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4 + 1.5\text{Fe}(\text{OH})_3(\text{s})$

II Cation exchange

(28) Iron	$\text{Ca-X}(\text{s}) + \text{Fe}^{2+} \rightleftharpoons \text{Fe-X} + \text{Ca}^{2+}$
(29) Protons	$\text{Ca-X}(\text{s}) + \text{H}^+ \rightleftharpoons \text{H-X} + \text{Ca}^{2+}$

Processes involved in acidity generation

III Redox/precipitation reactions

(30) Pyrrhotite formation	$2.25 < \text{CH}_2\text{O} > + \text{FeOOH} + \text{SO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{FeS} + 2.25\text{CO}_2 + 3.75\text{H}_2\text{O}$
(31) Sulfur formation	$1.5 < \text{CH}_2\text{O} > + \text{SO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{S}^0 + 1.5\text{CO}_2 + 2.5\text{H}_2\text{O}$
(32) Pyrite formation	$3.75 < \text{CH}_2\text{O} > + \text{FeOOH} + 2\text{SO}_4^{2-} + 4\text{H}^+ \rightleftharpoons \text{FeS}_2 + 3.75\text{CO}_2 + 6.25\text{H}_2\text{O}$
(33) Sulfate reduction	$\text{SO}_4^{2-} + 2 < \text{CH}_2\text{O} > + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O}$
(34) Iron reduction	$\text{Fe}(\text{OH})_3 + 1/4 < \text{CH}_2\text{O} > + 2\text{H}^+ \rightleftharpoons \text{Fe}^{2+} + 1/4\text{CO}_2 + 11/4\text{H}_2\text{O}$

Source: ¹Bigham et al. (1996b); ²Parkhurst (1995); ³Yu et al. (1999); ⁴Ball and Nordstrom (1991); ⁵Nordstrom (1982); ⁶Lindsay (1979); ⁸example composition.

Figure 1. Selected processes causing changes in acidity of mine waters (Blodau 2006).

The kinetics of oxygenation of pyrite depends on temperature, pH, partial pressure of oxygen, exposed surface, and the concentration of selected ions in the solution (Smith and Shumate, 1970).

At low pH values (2–3) the action of acidophilic sulphide-oxidising bacteria dominates the oxidation of pyrite in mine waters. Meanwhile abiotic oxidation of dissolved ferrous to ferric iron is fastest at elevated pH levels and, hence, in net alkaline waters with pH 6–7, this process should dominate (Banks et al., 1997; Johnson and Hallberg, 2005).

Temperature is also a significant factor. An increase in temperature increases the rate of sulphide oxidation, especially pyrite contained in coal waste. Oxidation of pyrite is an exothermic process. If oxidation occurs in a closed system such as dumping grounds, dissipation of heat released in the process is not effective and consequently temperature in the system increases oxygenation is greatly accelerated too in the presence of surfaces.



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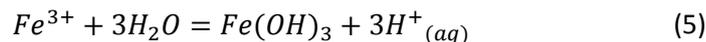
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3 Ochre deposits mechanisms

Ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions in aqueous solution occur in a wide variety of commonly encountered aquatic contexts such as incidents of “red water” in water distribution systems, iron deposit problems in drip irrigation systems, acid mine drainage problems, a diverse range of industrial water treatment processes and natural cycles in fresh and marine water environments.

In pH conditions greater than approximately 3.5, Fe^{3+} reacts in water to form $\text{Fe}(\text{OH})_3$ precipitates:



Over time, precipitates such as FeO and $\text{FeO}(\text{OH})$ may form from continual dissolution of the $\text{Fe}(\text{OH})_3(\text{s})$. Precipitates depend on the geochemical of mine waters, but in particular goethite, jarosite, ferrihydrite, and schwertmannite are the most common minerals that form these precipitates (Bigam et al., 1990, 1996 a,b; Regenspurg et al., 2004).

Clogging of pipelines carrying mine water has always been an issue. Ochre appears in mine water discharges mainly from the oxidation of dissolved ferrous iron and precipitation of red-brown hydrated iron (III) oxide (ferrihydrite).

There are two main mechanisms for ochre accumulation: sedimentation and accretion (Dudeney et al. 2003).

Sedimentation normally occurs as the gravity settling of suspended particles when linear flow velocities decrease to <1 cm/s. Particles smaller than 0.1 mm do not settle readily, but may be retained by flow restriction and aggregation. Gravity sedimentation generally yields a deposit of low solids content ($<15\%$), although slow consolidation may follow, and leads to relatively large volumes of sludge.

Accretion takes place when suspended particles impact with, and adhere to, solid surfaces in contact with the flow, e.g. pipe walls, corrugated plates of plate and frame heat exchanger (PHE) or other suspended particles. In particular, build-up of ochre in pipelines by accretion represents a major operational problem.

The accretion process also occurs via surface adsorption of ferrous ions and oxygen, followed by in situ oxidation – an example of surface catalysis. Particles apparently adhere or adsorb over a wide range of linear water flow rates, probably up to about 4 m/s in pipes. The product is a relatively consolidated deposit of higher solids content (typically 20– 25%), particularly in turbulent pipe flow which tends to dehydrate or dewatering the deposit. When pumping raw mine water, the thickness of deposited ochre may increase by about 1–2 mm per week.



Figure 2. Ochre deposit in mine water discharge in Barredo (Spain)



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4 Influences of hydro-chemical characteristics of mine water in the iron deposits

The spontaneous chemical oxidation of Fe(II) to Fe(III) by O₂ is a complex process involving meta-stable partially oxidized intermediate species, which ultimately transform into a variety of stable iron oxide end-products such as hematite, magnetite, goethite and lepidocrocite..

The exact end-product(s) formed depends upon environmental conditions among which are pH, temperature, solution composition and oxidation rate. Although in many practical situations the nature of the end-products is of less interest than the oxidation kinetics, it is difficult to find in the literature a description of all the basic steps and principles governing the kinetics of these reactions.

4.1 Influence of air oxidation of ferrous iron in mine water

Iron present in mine water will usually be dissolved iron(II), because of anaerobic conditions. Ferrous iron has a high solubility in water while ferric iron has a low solubility product. The solubility product of iron(III) hydroxide at 25 °C is $2.0 \cdot 10^{-39}$. So iron(III) easily forms iron hydroxide flocks. These precipitates form particles that can be visible in water.

The presence of oxygen can catalyse the oxidation of ferrous ion, leading to clogging or scaling of pipe walls and other parts in contact with water.

The transformation of iron takes place by means of two processes; oxidation and hydrolysis. In the presence of oxygen, iron(II) will be oxidised to iron(III) (Lerk, 1965). Because of the low solubility product of iron(III) hydroxide the iron(III) will quickly hydrolyse to form iron(III) hydroxide flocks.

The iron discharged in coal mine drainage is typically largely in the form of ferrous iron (Hedin et al. 1994). Above a pH of 4 (most coal mines), ferric iron is typically absent, due to rapid hydrolysis and precipitation.



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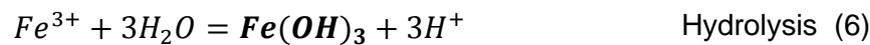
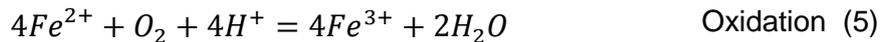
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On exposure to the atmosphere, ferrous iron will tend to be increasingly oxidised to ferric (which is highly insoluble above pH 2.5), accompanied by hydrolysis and partial precipitation as an iron oxyhydroxide (i.e ochre) (Banks et al., 1997). $Fe(OH)_3$ could be one of several amorphous or crystalline solids.



Special attention should be given to the kinetics of this reaction; the rate at which it proceeds depends on several parameters including pH, temperature, concentration of dissolved oxygen, and catalyst.

The rate of iron-oxidation has been studied extensively in the laboratory. Stumm and Morgan, 1996 suggested the rate law at near-neutral pH in the laboratory, and presented it as the following kinetic empirical equation for the oxidation of Fe^{2+} to Fe^{3+} with $O_2(aq)$ as the electron acceptor:

$$\frac{-d[Fe(III)]}{dt} = k [Fe(II)] P_{O_2} (OH^-)^2 \quad (7)$$

This empirical equation was derived by curve fitting techniques from data attained from the oxidation of oxidation of ferrous solutions of no more than 28 mg Fe/l, and at pH values between 4 and 6. In Figure 3.

In Figure 3. Oxidation rate of ferrous iron species as a function of pH

it can be seen that below pH 4 the rate of oxidation becomes very low, and is fundamentally independent of pH.

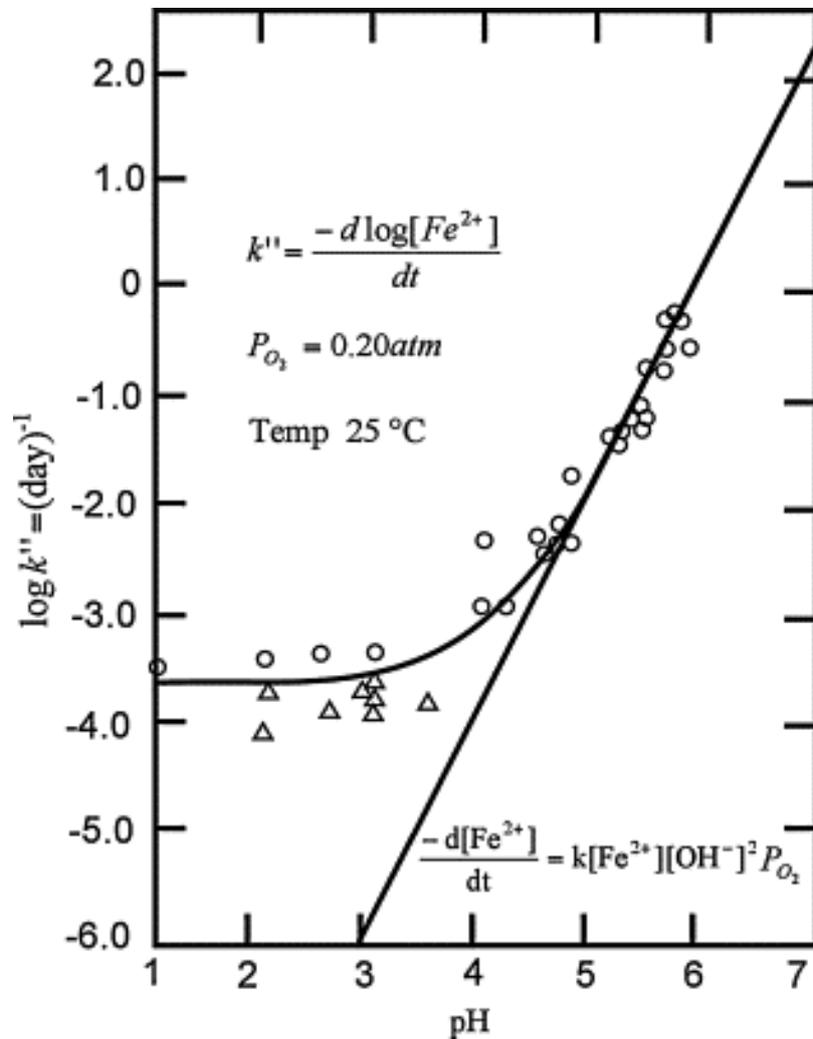


Figure 3. Oxidation rate of ferrous iron species as a function of pH (Singer, 1970)

Although microbially-catalyzed Fe oxidation rates are important at lower pH values (e.g., Kirby et al., 1999), they do not need to be considered at near-neutral pH values. Dempsey et al. (2001) and Dietz and Dempsey (2002) have shown that catalysis by Fe hydroxide solids can be important at near-neutral pH values, but such catalysis appears not to make a major contribution to Fe oxidation rates at low Fe solid concentrations. At pH between 7 and 8 the rate limiting factor governing the oxidation rate appears to be pH whereas at higher pH values, the dissolved oxygen (DO) concentration is the rate-limiting factor.

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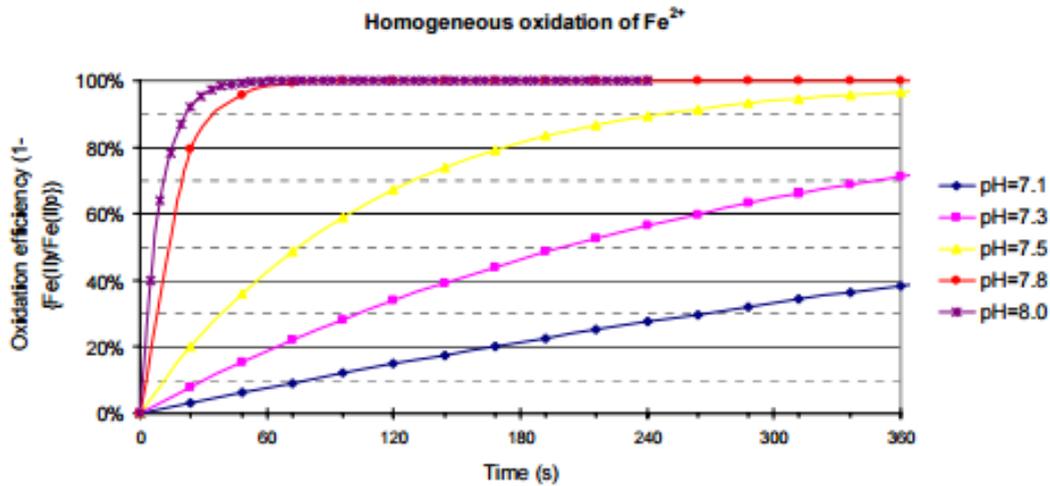


Figure 4. Oxidation efficiency of iron as a function of time at different pH values

Catalysts, like Cu^{2+} in trace quantities increase the reaction rate significantly, while small amounts of Fe(III) , Cl^- , SO_4^{2-} have no effect on the reaction rate.

Figure 5 shows the change in concentration with time of ferrous in aqueous solution as a consequence of oxidation by oxygen at different (constant) pH values.

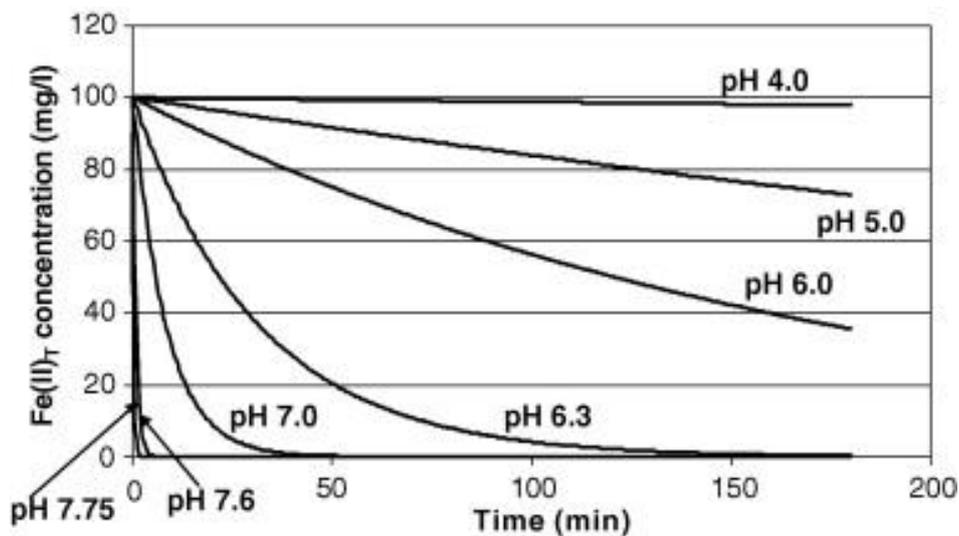


Figure 5. Oxidation rate of soluble Fe(II) in a batch test as a function of pH. Assumptions: infinite dilution and DO saturated at 25 °C. (Morgan & Lahav, 2007)

The stability of iron ion depends not only on pH but also on activity of electrons which is represented by a redox potential pE. High positive value of pE indicates oxidizing conditions where iron is insoluble and the low values of pE indicates reducing conditions where iron is soluble (Silveira, 1988).

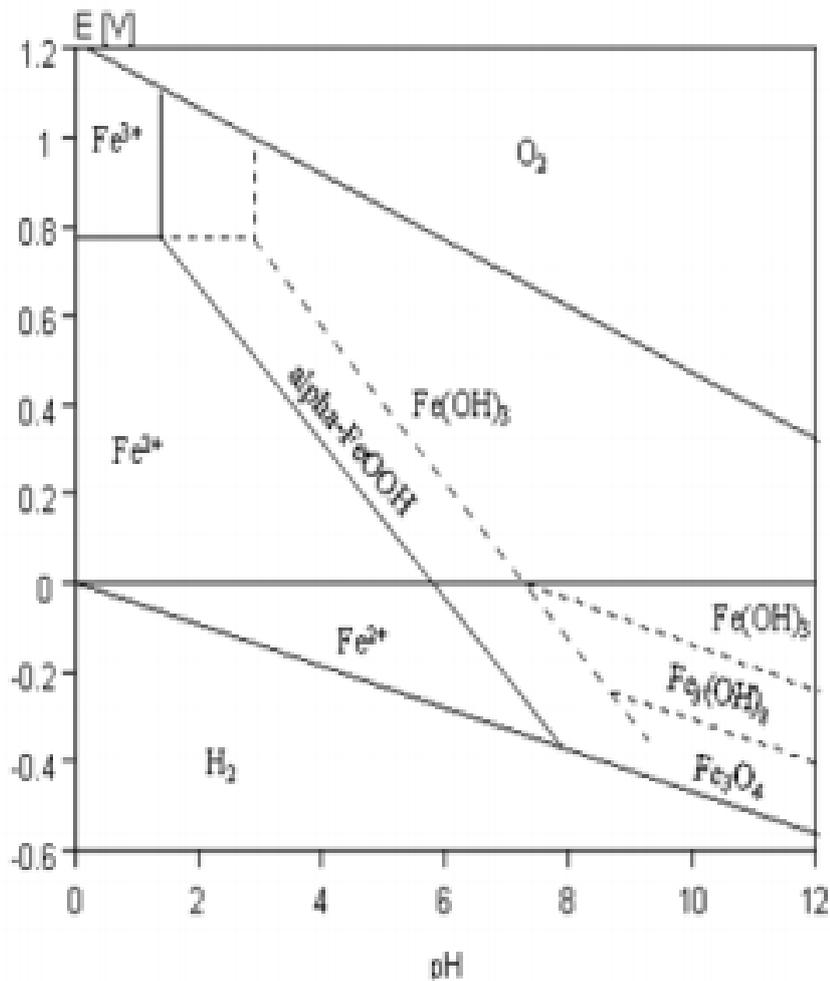


Figure 6 Eh-pH stability diagram iron

4.2 Influence of Carbon dioxide

Ground water and coal mine drainage commonly contain elevated concentrations of dissolved CO₂ in association with elevated partial pressures of CO₂ (Pco₂) of 10^{-1.5} to 10^{-0.5}



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as a thermal energy source - a baseline activity for minimising post-closure
environmental risks**



atm in the vadose zone and/or underlying saturated zone (Langmuir, 1997; Rose and Cravotta, 1998).

Elevated CO₂ concentrations contribute to the acidity and depress pH of AMD, but only temporarily (Kirby and Cravotta, 2005a, b); after the AMD emerges or has been sampled, the CO₂ eventually will degas until concentrations of dissolved CO₂ equilibrate with atmospheric Pco₂ of 10^{-3.4} atm (380 ppm v/v).

Mine waters can contain partial pressure of carbon dioxide in excess which tends to degas if exposed to atmospheric pressure or under-pressure. If CO₂ degassing occurs it tends to raise the pH of the water and increase the tendency for incrustation or clogging by, for example, calcium carbonate and iron oxyhydroxide.

5 Control of ochre clogging in geothermal applications

When using mine water as a geothermal fluid the risk of ochre clogging and accretion is increased as the fluid has to flow, not only through pipelines, but through the narrower and more tortuous heat exchangers, in order to deliver the heat.



Figure 7. Encrustations in a discharge pipe (Majkic-Dursun et al., 2015)

A way to reduce the rate of pyrite oxidation in the mineworkings is to maintain a constant water level at the pumping shaft (Banks et al., 1997). Pyrite will remain in a reduced state in the flooded area meanwhile oxidation will occur in the unsaturated parts.

The mine water quality increases as the depth decreases, conversely the temperature increases with depth, thus for choosing the pumping height a compromise between water quality and temperature has to be taken.

The pipe material can influence the grade of ochre clogging. Experiments have shown that compounds mixed into the plastic of a pipe increase or decrease the ability of ochre to stick to it e.g. tin compounds in the plastic made the ochre stick less while lead salts make it



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adhere nine times greater. Ochre becomes more adhesive as it ages and with low temperatures, above 15° C there is virtually no temperature dependence (British Columbia., 1988)

To keep pipes, pumps, plates of heat exchanger or other elements through which water mine passes clean, physical cleaning by ‘jetting-out’ or ‘pigging’ can be undertaken periodically. However, different forms of chemical cleaning by use of dispersants or reductive leaching products may also be possible.

A comparison between different techniques to control and prevent ochreous deposits is presented in Dudeney et al., 2003.

Method	Advantages	Disadvantages
Jetting	Well established and simple operation	Needs access via hatchboxes every 100 m, possible environmental hazard, problem with complicated pipe geometry
Pigging	Clean and simple operation	Needs launch and receiving equipment, possible scouring of plastic pipe surfaces, problem with complicated pipe geometry
Dispersion	Applicable regardless of pipe material or geometry	Needs dosing facilities for both dispersion and subsequent flocculation
Prevention	Applicable regardless of pipe material or geometry	Untried technology, needs new dosing equipment

Figure 8. Options for managing ochre accretions in pipework (Dudeney et al. 2003)

5.1 Physical methods to control ochre accretion

The control of the ochre accretion at the pipelines conveying raw mine water has been typically done by means of physical methods as jetting and pigging. Both are clean and simple to operate; however these physical methods are not suitable for pipelines which have complicated geometry, or other elements as some heat exchangers, and the need to access the clogged parts imply stopping operation which produces lost of performance.

Physical methods of jetting and pigging have been checked over several years at different mine water treatment sites. The process of high-pressure water jetting can remove a layer of up to 2–3 cm ochre but required several days of work, created ochreous contamination at surface and could not satisfactorily reach remote parts.

Pigging inlet system consists in inserting a pig – a composite foam and scraper construction shaped like a naval shell – into either pipeline via short detachable sections of pipe. Once re-

assembled and pumping, the pig is driven along the pipeline with the water flow (1–2 m/s), removing the surface layer of ochre in the process, and is caught in a net at the far end. Pigs of slightly different diameter allow the ochre to be removed in stages.

As access is required only at the beginning and end of the pipeline, the process successfully removes ochre without creating ochre spillage at surface. However, it needs carrying out more frequently (approximately monthly) than jetting, to avoid the possibility of a pig becoming wedged in thick ochre. The pigs also suffer damage, presumably on passage through the hatchboxes, around corners or at the outlet, and plastic pipework is probably subject to scouring, particularly on bends.

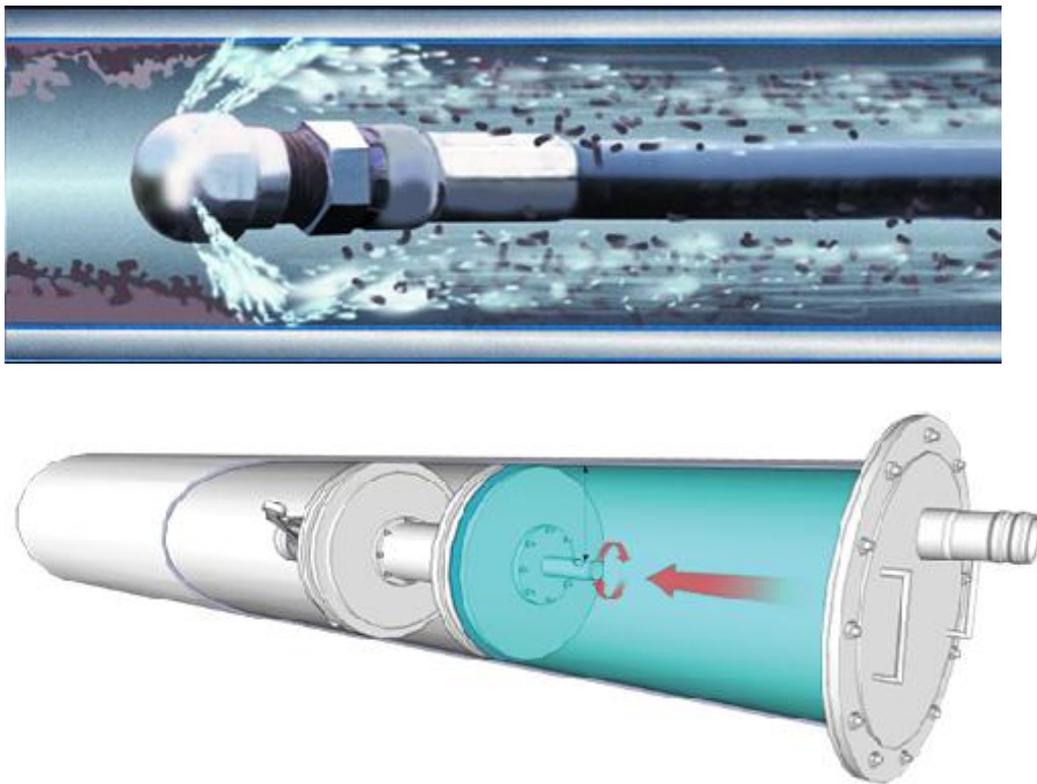


Figure 9. Jetting (upper picture) and pigging (lower picture) methods

Pigs are easier to use in pipelines, where are driven with the water flow, removing the surface layer of ochre in the process, and is caught at the end. Pigs can't be used in plate and frame heat exchanger due to the narrow and complicated paths to pass through.



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5.2 Chemical agents to prevent ochre clogging and scaling

Chemical disruption methods include the application of acids, ligands (i.e., chelators), or reducing agents directly to the mine water. Acids are normally not a recommended course of action, as more environmental and technical problems inevitably result. While decreasing the pH of the mine water here will encourage dissolution of the iron precipitate..

Chelating treatments, such as sodium citrate, oxalate, and EDTA (Ethylenediaminetetraacetic acid), are generally more successful agents for disrupting the precipitates. Chelators bind to ferrous iron that is present in solution to form more soluble complexes. However, chelating agents are unable to remove insoluble ferric iron, and do not address low pH issues.

Ochre accretion can be also controlled by reducing agents, that first removes residual dissolved oxygen and then reduces iron (III) to iron (II), increasing the solubility of the iron which may then flow through the system in solution (Dudeney et al., 2003).

Sodium dithionite dosing can, in principle, be used to keep pipelines free of ochre accretions by reversibly de-aerating raw mine water.

However, the reagent presents a number of problems: its high cost, it requires special dosing equipment to ensure an optimal dose rate, without the presence of a chelating agent, the free Fe^{2+} will bind with sulfides to precipitate additional pyrite; and it does not limit impact accretion or adsorption by suspended particles unless dosed in excess – under which circumstances subsequent ochre precipitation is inhibited.

Dosing with reductive leachants, e.g. sodium dithionite, has received little attention, even though the technique is used widely in other sectors of industry, e.g. in china clay bleaching, to convert ochreous deposits to soluble ferrous iron.

Actually, the reagent first removes residual dissolved oxygen and then reduces iron(III). The potential advantage is that a relatively small dose rate should be sufficient in many cases. This is because mine water emerging from underground is normally in a largely reduced state.

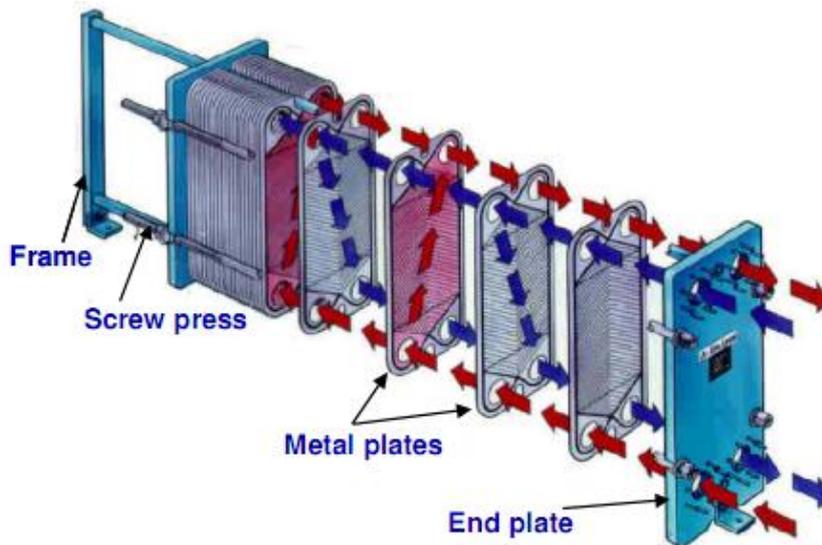


Figure 10. Plate exchanger (Courtesy of Nibley™)

Chemical dosing with phosphate-based dispersants may easily be dosed into a sump or injected directly into a pipeline and will undoubtedly remove ochre scale. However, the need subsequently to break the dispersion and sediment the ochre represents an additional cost.

Small quantities of technical sodium dithionite, dosed as a powder or solution to flowing mine water, rapidly scavenged dissolved oxygen and precluded iron oxidation and accretion, providing that the mine water was free of suspended particles. Thus, dissolved oxygen could be reduced to <10% of full saturation by means of about the theoretically required dose within a few minutes – much less than the normal residence time in the Bullhouse sump (1–2 hours) or pipeline (6–8 minutes). Larger quantities of reagent dissolved any ochre particles in suspension and could thus prevent impact accretion. Careful dithionite dosing in the range 12–100 mg/L mine water reduced the DO of the mine water efficiently to insignificant levels (<10%), even though passage through the sump had initially increased the raw mine water DO from 42% to 63–69% (Dudeney et al 2003). Larger quantities of reagent dissolved any ochre particles in suspension and could thus prevent impact accretion.

The dosing of Sodium dithionite (Sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4$) has been proved to be quite effective at removing scale (Obreza et al., 2011) as can be seen in Fig 10. This reagent

has been already reported for maintenance at micro-irrigation systems and is also used in the textile industry for the reduction of vat dyes and in the pulp and paper industry for bleaching (Ludwig et al., 2007).

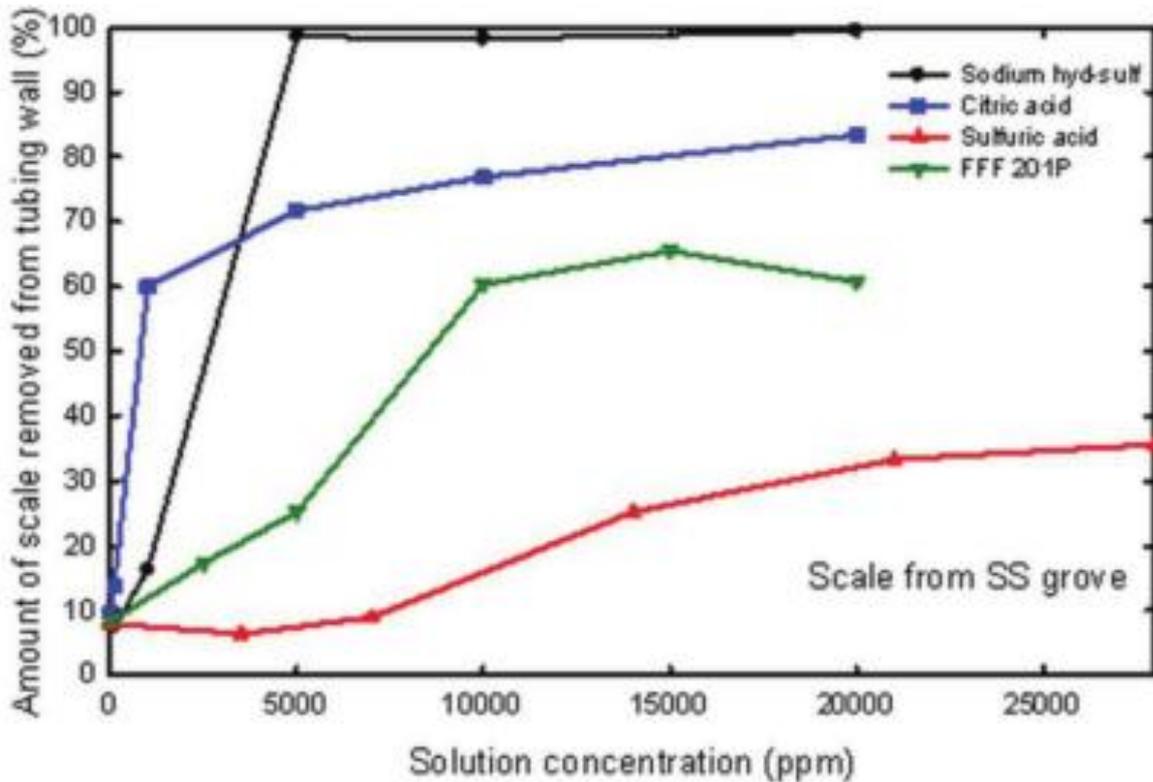


Figure 11. Efficacy of selected chemicals in removing iron scale from irrigation tubing (Obreza et al., 2011)

6 Experiences of clogging in geothermal open loop systems

At open loop mine water geothermal systems the build-up of ochre in pipelines, pumps and heat exchangers (accretion) represents the major operational problem as requires frequent stops of the installation for maintenance works that will decrease the efficiency of the system increasing the associated costs.

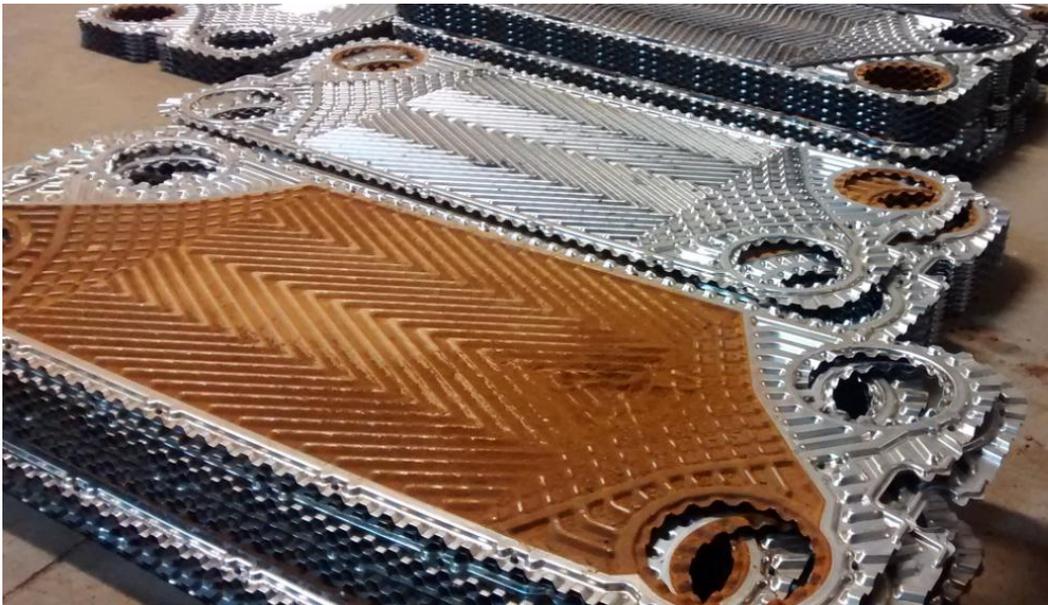


Figure 12. Heat exchanger before removing ochre at University of Oviedo geothermal installation

Fouling/clogging involves the formation and accumulation of unwanted materials on the surfaces of heat transfer equipment, which can deteriorate the capacity of the surface to transfer heat under the temperature difference conditions for which it was designed (Awad, 2011). Deposits create an insulating layer over the surface of the heat exchanger that decreases the heat transfer between fluids and increases the pressure drop, as a result of the narrowing of the flow area, which increases the gap velocity (Wang et al., 2009). Therefore, the thermal performance of the heat exchanger decreases with time, resulting in an undersized heat exchanger and causing the process efficiency to be reduced. Oversizing the equipment has proven not to be a solution, so the deposits must be removed by regular



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and intensive cleaning procedures in order to maintain production efficiency (Kananeh and Peschel, 2012). Described as the major unresolved problem in heat transfer, fouling is an extremely complex phenomenon where chemical, solubility, corrosion and biological processes may take place (Bott, 1995).

Water chemistry for hydraulic water-to-water heat exchangers is critical for a successful system. Water compounds should be kept under desirable levels, and in particular, gas contents (oxygen and carbon dioxide) must be controlled.

High levels of CO₂ and O₂ in the water will act to decrease the protective layer of minerals that form the surface of the heat exchanger, increasing the formation of metal oxides (MTS, 2005). In the presence of CO₂, anaerobic bacteria can cause corrosion and pitting by the reduction of sulphates into sulphides (Engineering page, 2017).

Corrosion fouling is strongly affected by the amount of oxygen dissolved in the water, which is also necessary for the maintenance of biological fouling. Corrosion fouling occurs when the surface of the heat exchanger reacts with the dissolved oxygen in the water so it is oxidized to produce corrosion products. These products then form deposits on the heat exchanger surface and promote the attachment of other foulants. The corrosion rate increases with temperature but it also requires the presence of dissolved oxygen; thus the dissolved oxygen content is critical at low temperature, as it is naturally reduced at higher temperatures due to the decreasing solubility of oxygen in water (Pugh et al., 2003). Additionally, low water pH (less than 7) combined with carbon dioxide or oxygen produces corrosion, with considerable effects on the heat transfer performance, particularly in the initial period (Xu et al., 2011; MTS, 2005).

It is recommended to have at least one spare heat exchanger to be used while the clogged one is being cleaned, this will minimise the stops of the system.



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6.1 Experiences in United Kingdom

Two open-loop, minewater-based, ground source heating schemes have been operating since 1999–2000 in Scotland (UK), at Shettleston (Glasgow) and near Cowdenbeath (Fife). In both cases, ferruginous water is pumped from flooded coal mine workings via a borehole, circulated through the evaporator of the heat pump and reinjected via a shallower borehole to Carboniferous strata.

The heat is delivered to a water-based thermal store providing central heating for apartment complexes and contributing to domestic hot water. It is demonstrated, via hydrochemical analysis and speciation modelling of the Fife minewater, that the success of the schemes is due to lack of contact between minewater and the atmosphere (thus limiting degassing of CO₂ and absorption of O₂).

Indeed, recent difficulties with one of the schemes are ascribed to vandalism of the recharge main allowing access to oxygen, causing precipitation of ferric oxyhydroxide and clogging of the recharge borehole.

6.2 Experiences in Spain: Barredo Case

Hunosa has reported that during five years after the flooding of Barredo Mine (Asturias) the chemical quality of the water was quite poor, with high concentration of ions (CaCO₃, SO₄, Ca, Fe, Mg, Na and K). Right now the quality of the water is better. It is usually considered that when the total volume of pumped water is six times the total volume of the mine reservoir voids, the quality of the water starts to improve.

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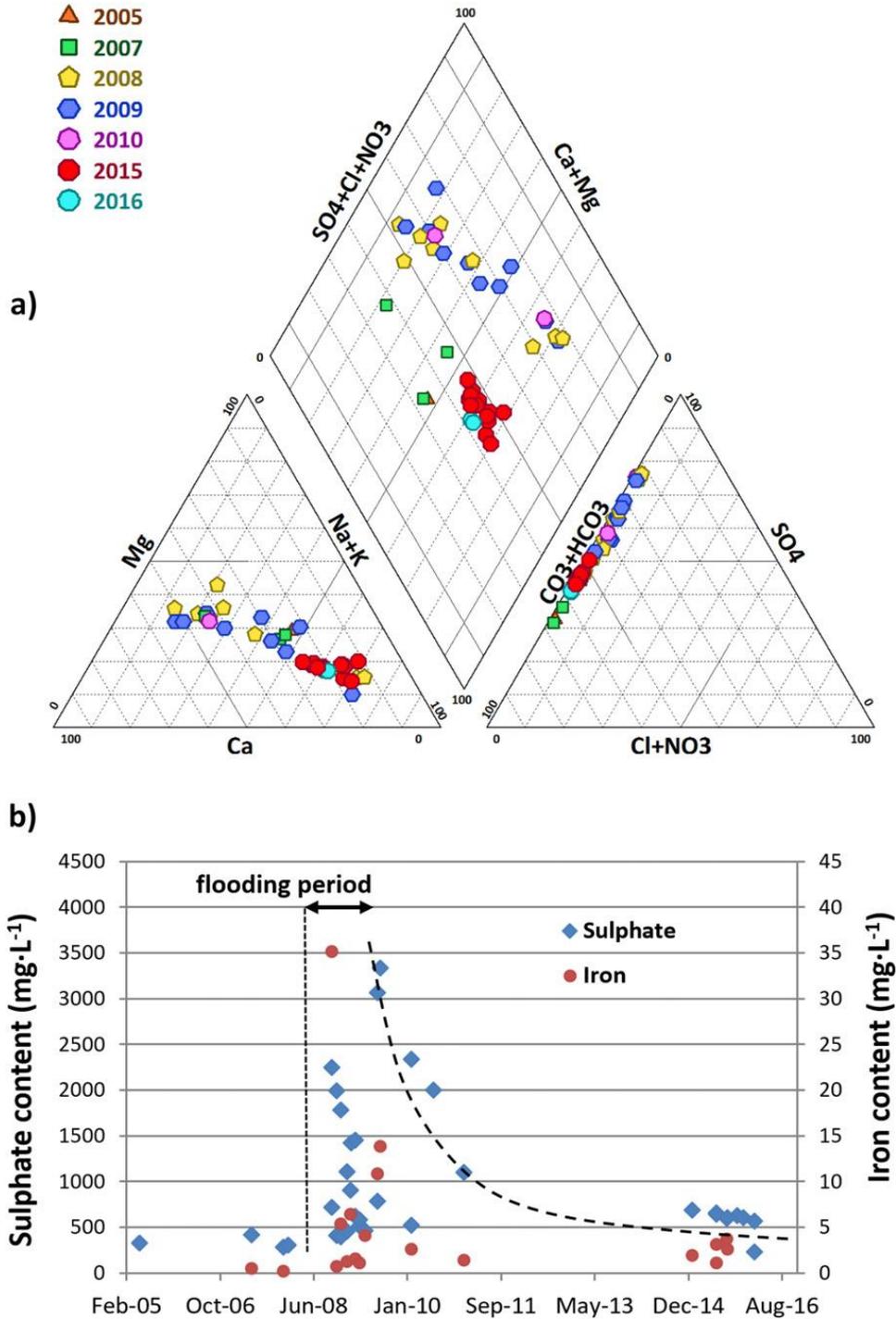


Figure 13. a) Piper plot of Barredo and Figaredo waters sampled from 2005 to present; b) Time evolution of sulphate and Fe content in Barredo and Figaredo waters. (C. Loredo, 2017)

Barredo and Figaredo mine waters can be classified as near neutral, high metal waters. and have high volumes of ions in solution. The mean content of dissolved Fe in Figaredo and Barredo waters at proximal depths, reaching up to 3.1 and 3.7 mg L⁻¹, respectively. A maximum concentration of 5.2 mg L⁻¹ was found in the water pumped from Barredo. It can be noted that Fe and Mn contents increase with depth.

When unfiltered samples are compared, total iron decreases by 62% in the heat exchanger, likely due to the deposition of suspended iron-rich particles.

The chemical reactions by which dissolved iron precipitates in the form of iron (oxy)hydroxides are well documented in the literature (Camden-Smith et al., 2015; Younger et al., 2002, among others). These Fe (oxy)hydroxides occur in anhydrous (FeO(OH)) or hydrated (FeO(OH)·nH₂O) forms. The so-called yellow Fe oxide corresponds to the monohydrate or ferric hydroxide (Fe(OH)₃). When Barredo water passes through the heat exchanger, it undergoes an average reduction of 23% in its DO (C. Loredo, 2017).

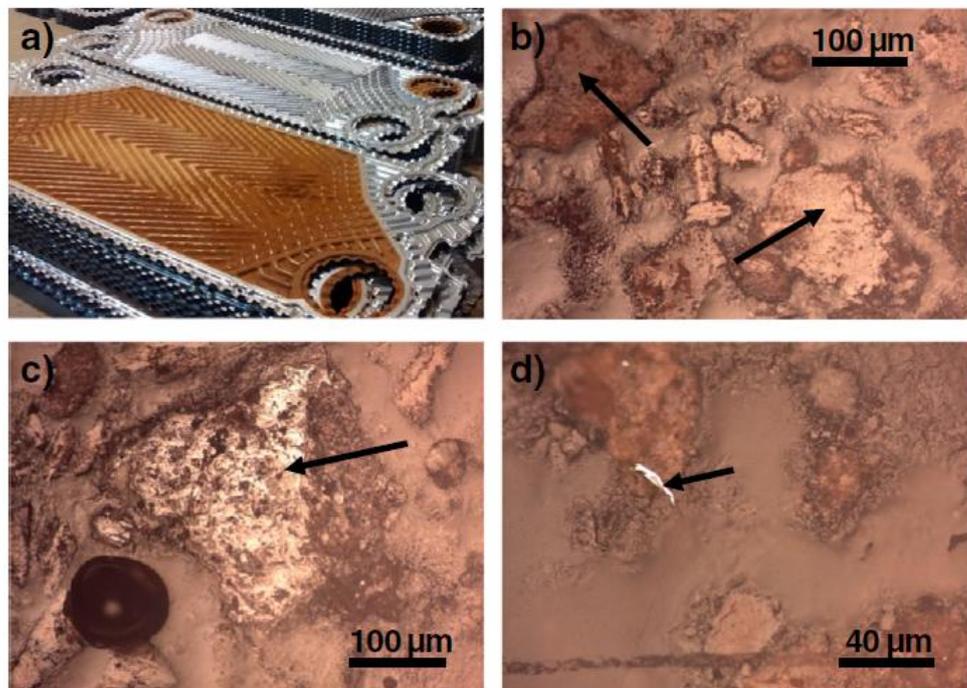


Figure 14. a) Deposits clogging a heat exchanger plate; b) grey and brown grains of the Fe oxide that constitutes the principal component of these deposits; c) goethite grain with colloform internal texture; d) pyrite particle with marked reflectance. Images b, c and d taken with reflected light (parallel Nicols).

(C. Loredo, 2017)



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Mine water TDS is higher than desirable for optimal heat exchanger performance. The solubility of dissolved minerals is affected by changes in temperature within the heat exchanger and chemical reactions between compounds found in the water. In particular, the iron content and hardness of the water are largely responsible for the precipitation of Fe (oxy)hydroxides on the heat exchanger (Fig. 6a). The origin of common iron compounds in coal mine water are well known: pyrite oxidation generates Fe^{2+} which undergoes oxidation, releasing Fe^{3+} , and if Eh/pH are adequate, the ferric ion precipitates as ferric hydroxide ($Fe(OH)_3$) (Camden-Smith et al., 2015). As it was previously stated, a pH increase nudges the chemical reaction equilibrium in favour of ferric hydroxide precipitation. The effect of temperature, in K_{eq} of this reaction is difficult to specify, as ferric oxyhydroxide can take a number of forms (amorphous, microcrystalline), but Appelo and Postma (1996) suggest an absolute value of: $K_{eq}=10^{-4}$. In this case, the temperature of the influent is slightly decreases after flowing through the exchanger, but the effect of the pH (a “master variable”) increase is more critical than that of the temperature.

X-ray fluorescence and optical microscopy studies showed that the precipitates sampled on the exchanger are mainly amorphous iron oxy-hydroxides, containing up to 6.3% of $CaCO_3$ and minor concentrations of Mn oxide. Only a minimal portion of crystalline goethite [α - $FeO(OH)$], was identified by X-ray diffraction. When observed by optical polarizing microscopy, the major constituent of the heat exchanger deposits is a grey/brown non-crystalline layered soft component (Fig. 13b), which is an iron oxide. Goethite is common but not frequent; it appears in individual grains of irregular morphology and shows marked colloform internal textures and a grain size up to 200–300 μm (Fig. 13c). Dispersed sub-angular, well preserved pyrite grains 20–50 μm in size are present as individual particles. These differ from the above minerals because they do not originate by precipitation from the mine water and are likely to have been transported in suspension to the sampling point (Fig. 13d). These particles are a component of the suspended solids captured during the precipitation process (a Scanning Electron Microscope analysis would confirm this). This result is in agreement with the reduction of Fe content in unfiltered samples after passing through the heat exchanger. Therefore, we suggest water filtering and regular cleaning of the heat exchanger will be sufficient to keep the fluid velocity high enough to inhibit scaling and clogging.

The precipitation of sulfates and carbonates of Fe, Ca and Mg causes a lot of problems to the conductions and pipes of the mine water. The Figure 15 shows an example of the depositions inside a pumping pipe. This precipitation is higher when the oxygen of the air reaches the water just when it is pumped. The redox of this water is negative, so the iron is in form of Fe^{+2} , once this water gets the air, the iron quickly is oxidized to Fe^{+3} with low solubility, and the precipitation starts.



Figure 15. Depositions inside a pumping conduction

The effects of iron precipitation can go far from the pumping station, in case of calcium the precipitation occurs closer, and usually cause the erosion of the pipes so is need to change them, especially the curved ones.

In the case of the Research Centre of the Oviedo University in Mieres Campus, the mine water is pumped from HUNOSA Barredo shaft directly into the installation of the university. Two plate heat exchangers were installed and due to the risk of carbonates and ochre precipitation a maintenance program was defined, in order to avoid the reduction in the efficiency of these heat exchangers. According to the concentration of iron a maintenance

program of at least three times per year to clean the heat exchangers was established. The following images show how the equipment was the first time it was cleaned.



Figure 16. Filter before cleaning.



Figure 17. Filter after cleaning.

7 Lesson learned for clogging prevention

From the experiences that have been studied, several strategies can be applied to avoid the ochre clogging problem in mine water geothermal systems :

- Reduce the circuits with mine water. The heat exchanger should be placed as close as possible to the shaft, so the most part of the installation works with clean water. This can reduce the efficiency of the system but also the maintenance. This is the case of the project for the Mieres Hospital. The distant between the hospital and Barredo Shaft is 2 km, it would be unavailable to use the mine water directly along 2 km of pipes. In the final design the exchanger is just near Barredo Shaft and there is a close-loop circuit with two pipes of 400 mm of diameter full of clean water that transport the heat between the hospital and the mine water.



Figure 18. Heat exchanger in Barredo Shaft

- Use tubular heat exchangers instead of plate exchangers. In the tubular exchanger the water can go so quickly that avoid the precipitation of solids. This is the design principle for Hospital and FAEN projects. The idea is to avoid the precipitation inside the pipes, so the exchanger efficiency keeps constant. In the Figure 19 it is shown the efficiency and dirt accumulation comparison in tube and plate heat exchanger. It is easy to see that although the plate exchanger seems to be better at the beginning in only 500 hours, due to the quickly accumulation of dirtiness, the efficiency of the plate

heat exchanger drops so it is necessary to clean the exchanger, otherwise it would be useless. When this exchanger is installed in a geothermal project this efficiency loss can cause a great loss of the COP and ERR of the heat pump so the heat pump requires more electricity to give the same heat.

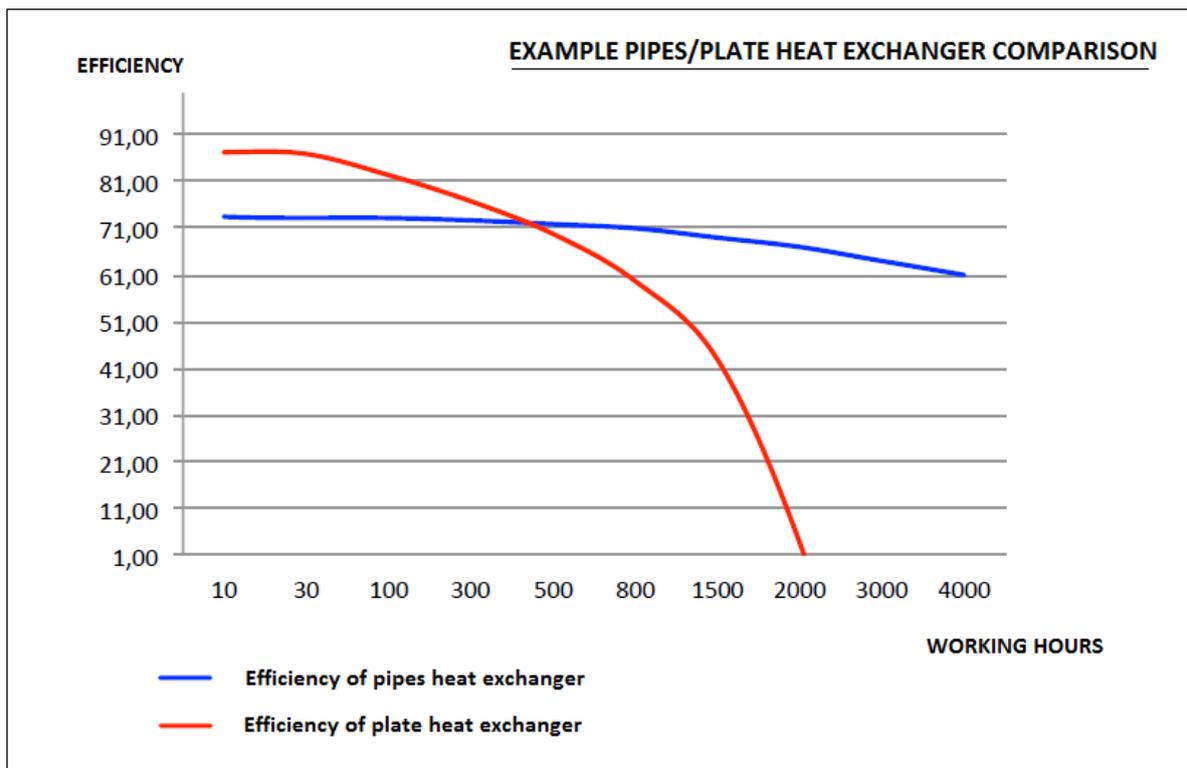


Figure 19. Efficiency of heat exchanger in time (HUNOSA)

- Reduce the possibility of the oxygen to reach the mine water and to prevent the CO₂ degassing. This is easy to achieve, all the pumps are immerse under the water level, and the water goes directly to the heat exchanger, as have been observed in the cases of UK mines and Barredo mine.
- Maintain the water levels as constant as possible. The objective of this measure is to avoid changes of redox in the groundwater that helps to put minerals in solution.



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