MATERIALS FOR VOLCANIC ENVIRONMENTS - WHERE WILL THE DATA COME FROM

K. A. LICHTI AND G. MCILHONE

Scientists, Industrial Research Limited, Lower Hutt, New Zealand

SUMMARY - The chemical composition of high temperature volcanic-magmatic environments is dominated by the presence of corrosive gases CO_2, SO, H_2S, HCl and HF. Materials performance data for such high temperature *mixed* gas environments is not readily available. Energy development plans for the utilisation of these environments have also not yet been formulated and hence physical and chemical conditions of exploitation cannot be fully defined. Corrosion results are being obtained for natural volcanic environments at atmospheric pressures to develop models of corrosion processes and establish materials performance rankings. Industrial experience with high temperature environments, for example in high temperature combustion plant, containing one or two of these corrosive *gases* are available and this knowledge *can* assist materials engineers in formulating models of corrosion. Similarly, experience and corrosion testing results in aggressive aqueous systems, such as flue *gas* desulfurisation systems, containing dissolved or condensed derivatives of these gases, can be used to define materials suitable for handling and disposal of waste waters and low temperature condensates.

1 INTRODUCTION

The development of so-called "deepseated" geothermal reserves is now being promoted and evaluated for Japanese geothermal systems and other fields around the world (NEDO, 1994). Deep drilling to depths in excess of 2,500 m in proven geothermal fields gives an opportunity to enlarge current reserves in a vertical direction. Although deep drilling may be more difficult, the savings in new resource development costs are considered *significant.* Temperatures of 350 to 400°C at depths of 4,000 m are expected to be reached before the year 2000. The deep reserves in Japan are estimated to be c. 43,000 MWe, twice that of conventional shallow reserves (Sasada et al, 1994).

A natural extension of this deep drilling philosophy has been the discussion of options for drilling close to magma with a view to utilising these "magma-ambient" high temperature (400 to 800°C) systems for energy production (Muraoka, 1994). White Island, New Zealand has been suggested as a prime site! for such investigative drilling as the magma is believed to be less than 1000 m below the surface (Giggenbach, personal communication).

The chemical composition of fluids derived from deep *seated* and magma-ambient hydrothermal systems is governed by the magma degassing processes and the properties of the surrounding reservoir (see Section 2 below). A major factor controlling the chemical environments encountered in magma-ambient energy developments, will be the choice of energy utilisation system and this will affect the materials options. Conventional wells can intercept magnetic-hydrothermal environments at depths as low as 1600 to 2200 m and the resultant acid-pH fluids do cause materials problems (Reyes, personal communication).

11 Plant and Materials Options

In conventional geothermal systems the main plant construction materials are carbon and low alloy steels, 12% Cr stainless steels and austenitic stainless steels. High alloy stainless steels and nickel-base alloys are only used in applications where *greater* reliability and/or freedom from corrosion product scale formation is essential.

Deep-seated wells are expected to produce fluids consisting of vapour and liquid phases in a similar manner to wells drilled into the shallower parts of a geothermal reservoir. Minimal change in plant and equipment is predicted for deep-seated magmatic-hydrothermal systems, although fluid handling practices, plant operation and materials selection may have to allow for greater potential for thermal *shock* with *higher* downhole temperatures, and increased fluid scaling and corrosion properties at the higher temperatures encountered.

Energy utilisation systems for the higher temperature magma-ambient systems have not been fully defined or explored. Plant and equipment options will be influenced by environment characteristics and predictions of reservoir response to exploitation. The chemical environments expected for some parts of the plant will be sufficiently aggressive to require alloys which are more resistant to corrosion than the conventional materials presently used for geothermal plant. Alloys having improved high temperature mechanical and corrosion properties such as high alloy stainless steels and nickel-base alloys will be required.

These same high temperature corrosion resistant alloys as well as titanium alloys and non-metallic materials *can* be considered for low temperature environments where acidic condensates must be handled or otherwise treated. The expected high cost of these materials justifies testing in actual and simulated environments to define the most economic alloys having sufficient but not excessive resistance to corrosion.

Materials *cost* will undoubtedly be greater than expected by developers and will become a major factor in determining the type of energy extraction process and plant utilised. Plant which *can* handle the aggressive fluids will need to be small in comparison with conventional geothermal *systems*, eg heat exchangers located at the wellhead or downhole, rather than long pipelines. Downhole heat exchangers for magma-ambient systems are being investigated (Morita and *Tago*, 1994). *An* advantage of such a system would be avoidance of the need to produce and dispose of aggressive volcanic fluids, but again the effects of heat removal from a magnetic-volcanic reservoir on the local chemical environment and materials options have not been defined.

2. CHEMISTRY OF VOLCANIC ENVIRONMENTS

Volcanic environments have been studied with a view to predicting or explaining volcanic activity (see for example Giggenbach et al, 1990). The chemical composition of volcanic systems is dependent on the age of the cooling solidified magna and the gas-water-rock reactions taking place within the reservoir. The majority of measured gas and water chemistries for such systems are for fumaroles and other natural surface discharges. Wells which produce acidic fluids have also been characterised (Reyes, 1990). Pressurised reservoir conditions next to solidified magma cannot presently be accessed but the undisturbed chemistry of these regions which contain magmatic-volcanic gases can be inferred (Giggenbach et al, 1990; Muraoka, 1994). Although possible local chemical environments of magma-ambient energy developments have not been investigated these will include chemical environments similar to those encountered in:

- dry steam fumaroles
- wet steam fumaroles
- acid pH *springs*, pools and streams
- drilled wells producing acid pH fluids.

High temperature *dry* steam and gas in fumaroles *can* be at temperatures as high as 800°C. The gases contained in these environments *are* derived from degassing of solidified magma Some of these *gases* may be dissolved in and reacted with local brines which subsequently react with the surrounding rock. Reheating of brines which have dissolved some of these gases will again release the gases (Giggenbach and Sheppard, 1989; Giggenbach et al, 1990; Shinohara *et* al, 1993). Magmatic and derived gases may include:

- water vapour as *dry steam*, H_2O
- *carbon* dioxide, CO_2
- sulfur *gases*, SO_2 and H_2S
- hydrogen halides, HCl and HF
- ammonia, NH_3
- hydrocarbon, ie CH_4
- hydrogen, H_2
- inert gases, *Ar*, N_2

Concentrations of these will vary but the high temperature *dry gas* corrosion chemistry of the atmospheric pressure environments will be determined by the concentrations of sulfur and hydrogen halides as well as the concentration of any oxygen drawn into the local environment.

Wet steam fumaroles will contain the above gases but have the addition of steam condensate at atmospheric pressure and temperatures approaching 100°C. The aqueous corrosion chemistry of these environments will be severe due to the dissolved sulphur and hydrogen halides and natural aeration.

Acid pH springs, pools and streams will have temperatures as high as 100°C and pH values which maybe less than 1. Their cornsion chemistry will be determined not only by the level of dissolved *gases* but also by *the* salinity of *the* water. As chloride concentration is increased the corrosion chemistry will become more severe. Aeration will also effect corrosiveness of these solutions.

Drilled wells producing acid pH fluids will have corrosion environments controlled by the presence of hydrogen halides, HCl and HF, or the presence of Corrosive *sulfur* species (Reyes, 1990). These wells may intercept magmatic-volcanic areas and the codon environments are believed to closely represent the characteristics of high temperature reservoir brine located close to the cooling solidified magma (Reyes, 1994).

3. CORROSION DATA SOURCES

Materials performance results for volcanic energy environments would ideally be obtained in actual or simulated conditions but in the absence of such environments work *can* be done to establish material performance ranking and to define corrosion mechanisms for available environments. Existing data for similar environments *can* also be reviewed to define problems and solutions in other industrial applications (McIlhone, 1994).

31 Research *in* Volcanic Environments

Corrosion research in readily available magmatic-hydrothermal environments has been initiated and results for materials exposed to fumarolic environments are becoming available.

Exposures tests at Kuju-Iwoyama, Japan were conducted with a range of alloys exposed in a test chamber containing *dry* steam and *gas* derived from a fumarole (Saito et al, 1994). The temperature of the test was 233°C. Gases present included: 97.58% H_2O, 1.4% CO_2, 0.75% H_2S, 0.24% SO_2, 0.03% HCl and 0.01% HF. Results *suggested* that in this superheated environment corrosion of carbon and low alloy steels was similar to that observed in conventional geothermal systems while martensitic and austenitic *stainless* steels corroded at 2 to 3 times the rate found in conventional systems. Overall the corrosion of all materials tested was low and acceptable.

Exposure tests at White Island, New Zealand were conducted directly within a fumarole at a temperature of approximately 210°C (Kurata et al, 1994). Gases present included 90.6% H_2O, 9.1% CO_2, 0.5% H_2S, 0.4% SO_2, 0.0009% HCl and 0.0001% NH_3. "he corrosion in this environment was severe. Martensitic and ferritic (13% Cr) alloys and nickel base alloys which were low in Mo had corrosion rates in excess of 1 mm/y, compared to 0.5 to 0.8 mm/y for carbon steels. Nickel-base alloys with 3 to 8% Mo showed improved performance with corrosion rates of 0.1 to 0.6 mm/y whilst only the nickel base alloys with *greater* than 8% Mo, and titanium alloys corroded at less than 0.1 mm/y (Kurata et al, 1995). These authors suggest that Ni, W and Co are beneficial in this environment whereas Al, Si and Cr are deleterious. The reasons for the more aggressive nature of the White Island fumarole compared to the tests in Japan have not yet been determined.

High temperature brine environments encountered in conventional system where acid pH fluids are produced may have a chemistry similar to magma-ambient brines. The produced brines tend to corrode carbon *steels* at unacceptable rates. Wells having these aggressive chemistries have not been used for production although some wells are suitable far reinjection (Reyes, 1991). In flowing steam/water environments of moderate pH containing HCl, duplex stainless steels of the type UNS S31803 have been shown to give acceptable performance (Ikeuchi et al, 1982). Research into codon problems in high salinity environments (>129,000 ppm Cl) may assist in selection of materials for these environments (*see* for example Cramer et al, 1983).

High pressure, high temperature aqueous environments which will develop within the reservoir have not been targeted far research as the nature of these fluids under energy extraction conditions has not yet been defined. The corrosion chemistry of these environments is expected to be more severe than that encountered in aqueous high pressure, high temperature industrial process plants. However, once the chemistry is defined, guidance on materials *can* be sought from the relevant corrosion literature.

3.2 High Temperature Gaseous Atmospheres

For high temperature gaseous volcanic environments there are two areas that *can* provide useful guidance in the selection of materials: studies in gaseous environments, and experience from the *"dirty"* environments associated with combustion of fossil fuels and municipal refuse.

Gaseous environments which cause high-temperature corrosion problems encountered in industry can be attributed to the following modes of corrosion (Lai, 1990):

- oxidation
- carburisation and metal dusting
- nitridation
- halogen corrosion
- sulfidation
- ash/salt deposit corrosion
- molten salt corrosion
- molten metal corrosion.

In volcanic environments the most likely degradation mechanisms will involve halogens and sulfur *species* at various oxygen potentials, although the other modes of corrosion noted by Lai cannot be ignored. Kane and Taraborelli (1993) summarised the effects of halogens and sulphur species (amongst others) and possible alloy modifications to overcome likely problems as shown in Table 1.

Industrial combustion plant (boilers) fired using coal, oil, or refuse as a fuel experience high temperature corrosion which is *caused* by "impurities" in the fuels (Wright, 1987: Daniel et al, 1988):

- Coal: sulfur (≤ ≈ 5%), sodium and potassium (≤ ≈ 0.7% each), and chlorine (I≈ 0.3%).
- Oil: sulfur (≤ ≈ 4%), sodium (≤ ≈ .03%) and vanadium (≤ ≈ 0.015%).
- Refuse. chlorine (I≈ 0.7%), sulfur (≤ ≈ 0.15%), heavy metals (Fe, Cu, Zn, Pb, Sn etc) (≤ ≈ 12%)

Table 1- Corrosion problems and solutions in high temperature industrial plant (Kane and Taraborelli, 1993).

Impurity/ Contaminant	Corrosion mechanism	Alloying modification	Process changes
Carbon	Carburization	Add Cr, Ni, Si Add Al to Ni alloy	Decrease carbon activity Add O_2, H_2O or S
Nitrogen	Nitridization	Increase Ni (any Cr) Add Al to Ni alloy	Decrease temperature Decrease N compounds
Halogen gases (Cl, F, Br, I)	Formation of volatile metal halides on surface	Cl - Add Cr and Ni or use Ni+Mo alloys F, Br, I - Ni+Mo alloys	Know oxidation or reducing capabilities of environment
Sulfur species (H_2S, S, SO_2 etc)	Sulfidation	Add Cr, Mo Add Ni (less effective)	Avoid substoichiometric combustion
Ash/molten salts	Formation of molten salt deposits	Add Cr, Ni (up to 50Cr-50Ni)	Add MgO to control formation of molten *salts*

The presence of these impurities results in the formation of ash and salt deposits. Within and beneath these deposits corrosive environments are established, and corrosion proceeds by mechanisms such as sulfidation, oxidation, attack by hydrogen chloride, and corrosion and fluxing of protective surface films by molten salt eutectics. Both the metal temperature and the combustion gas temperature are important, and these temperatures limit the application of any particular alloy.

Selection of engineering materials in critical areas is limited to materials covered by boiler codes such as the ASME boiler code, which, in turn limit the design temperatures of the boiler. Materials allowed by the ASME boiler code are specific carbon, ferritic alloy, and austenitic stainless steels. Materials which have been used successfully in these environments are summarised in Table 2.

3 3 Flue Gas Pollution Control

Application of air pollution control measures to boiler and incinerator flue gas emissions has become necessary to meet international standards for control of acid rain. Flue gas treatment processes and materials for handling the corrosive solutions have been under development since the 1970's with an increasing level of activity in alloy development in recent years. In many situations flue gas containing SO_2, HF, HCl, HBr as well as particulate matter is quenched to moderate temperatures before treatment and the resulting liquids are corrosive. Developed processes, materials experience and construction techniques could, with some provisos be applied to the handling and disposal of non-condensable volcanic gases and acidic condensates.

Materials used include (Ladwein, 1992):
- rubber linings
- polyester coatings
- acid resistant brick linings
- corrosion resistant stainless steels
- corrosion resistant non-ferrous alloys.

Life cycle cost considerations have provided economic justification for selection of the more corrosion resistant metallic materials. This is due in part to development of improved cladding and "wallpapering" practices for these alloys.

Corrosion resistance ranking of nickel-base alloys for example in aggressive aqueous environments suggests (Agarwal et al, 1993):

Best	Alloy 59, C-276, C-4, C-22
Good to Adequate	Alloy 625, 31, 1925hMo, G-3
Borderline	Alloy 904L, 28,825
Unsatisfactory	Alloy 304L, 316L

The cost differences of these alloys would justify investigating their performance in aggressive low temperature volcanic environments prior to alloy selection.

4. THEORETICAL AND PRACTICAL MODELS

The corrosive species and corrosion product phases that will be stable in both high and low temperature systems can theoretically be predicted by the use of thermodynamics.

Table 2- Materials successfully used in boiler environments.

Fuel	Item	Material*	Comments
Coal/oil	Conventional boiler tube and superheater tube	Carbon steel Low alloy steel AISI 310 50Cr-50Ni	AISI 310 and 50Cr-50Ni used as co-extruded tubing over carbon steel.
	Fluidised bed superheater tube	AISI 304347 AISI 310 Alloy 800	AISI 310 co-extruded over carbon steel. Alloy 800 restricted to regions having consistently high oxygen potential.
	Gas coolers in coal gasification plants	Low alloy steel High-Cr austenitic stainless steels.	Low alloy steels with aluminised or chromised coating. Austenitic stainless steel co-extruded over low alloy steel.
Refuse	Boiler tube	Carbon steel Low alloy steel AISI 304 AISI 310 Alloy 625 SiC	AISI 304,310 used as co-extruded tubing; alloy 625 as weld overlay; SiC as tiles or monolithic coating - over carbon steel
	superheater tube	Carbon steel Low alloy steel Alloy 825	Experimental alloys containing Fe, Ni, Cr with Mo, N and Co, Si also being tested commercially.

* Materials listed with alloys having greater resistance to corrosion towards the bottom of the list.

Because of the complexities of the systems involved, calculations are usually performed using computer programmes (see for example Besmann, 1977), and the results presented in the foam of a summary diagram in two dimensions. As the complexity of the systems increase, individual variables must be fixed, and a range of diagrams drawn to cover all possibilities. Aqueous Fe-H_2S-H_2O Pourbaix diagrams have seen extensive use in conventional geothermal systems (Lichti and Wilson, 1983). Some of the diagrams that have been utilised for high temperature gaseous applications are listed below:

Variation of AG with temperature
- One metal and one gas (Ellingham diagrams)

Isothermal phase stability diagrams
- One metal and two gases (Kellog diagrams)
- One metal and more than two gases (Darken diagrams)
- Metal alloy elements and several gases.

Potential-temperature diagrams
- "Gaseous" Pourbaix diagrams.

An example of a "Gaseous" Pourbaix diagram for the O-S-Fe system is shown in Figure 1 (Pourbaix and Zhang, 1988).

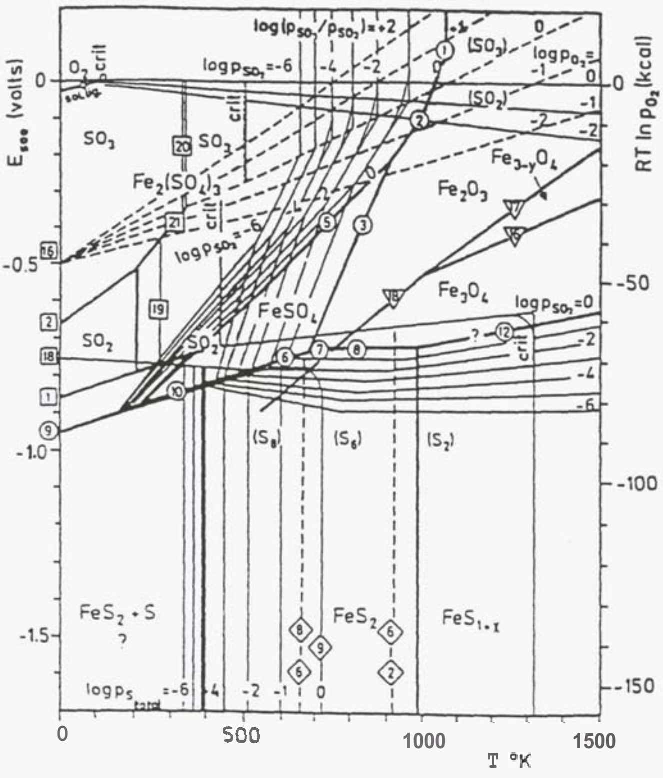

Figure 1- System O-S-Fe. Equilibrium diagram E_{sce} = f(T) (Pourbaix and Zhang, 1988).

At the high temperatures involved, kinetics of the reactions are such that equilibrium is reached relatively quickly. The diagrams can help in identifying alloy systems where a stable protective film will be formed, which will limit cornsion to acceptable values.

Other considerations, however, are important and can have an effect on the corrosion process, these include:

- localised environments (eg within crevices and cracks) that are not typical of the bulk environment
- start-up and shutdown conditions leading to atypical environments
- flow rate effects
- erosive particles
- applied or residual (tensile) stresses or fatigue loading
- rapidly fluctuating chemistries
- bimetallic contacts.

5. RESEARCH PROGRAMME

Materials research work in volcanic environments is expected to continue to concentrate on both high and low temperature natural volcanic features with the results being critically reviewed in terms of existing theoretical models and corrosion experience in similar industrial environments. These efforts will extend understanding of corrosion mechanisms and provide evidence for materials ranking. Final materials selection for energy developments will require confirmation of predicted performance in environments which more closely resemble the expected conditions.

Chemical conditions encountered in acid-pH wells where the acidity is predominantly due to sulfur species have been sufficiently well defined to permit laboratory simulation and materials testing to be considered as a means to identify suitable materials.

6. CONCLUSIONS

Volcanic-magmatic environments which might be encountered in a magma-ambient energy development will contain corrosive gases CO_2, SO, H_2S, HCl and HF. The local chemical environments cannot yet be defined as energy extraction plans have not been formulated. However, it is likely that materials used in conventional geothermal plant will have insufficient resistance to corrosion in these new environments. To minimise cost, and maximise safety, information is required on the performance of construction materials in these more corrosive environments.

Theoretical models of corrosion are being reviewed with a view to adapting these models to volcanic environments. Testing of developed models can be undertaken far readily accessible environments where corrosion data is more easily obtained.

Materials testing in atmospheric pressure volcanic features has begun with materials performance rankings being developed for high temperature dry steam and gas environments not previously tested. These results can be compared to experience from similar environments in industrial plants to aid the understanding of corrosion mechanisms and assist in the ranking of materials performance. Final materials selection and specification must await access to exploitation environments to verify the suitability of developed materials performance models.

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