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IEA Deep Geothermal Resources Subtask C: Materials, Progress with a Database for Materials Performance in Deep and Acidic Geothermal Wells

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ABSTRACT

The IEA Deep Geothermal Initiative, Subtask C on materials has been progressed by surveys of deep geothermal well experience and research results. This work revealed that the chemistry of deep geothermal fluids is expected to be more acidic than is encountered in conventional shallow reserves. Emphasis of collaborative research under Subtask C has been on volcanic environments which reflect the anticipated deep fluid chemistry and on a limited number of shallow wells which encounter and produce acidic fluids. The IEA sponsored meetings have facilitated additional sharing of results from previous acid fluid research and development activities.

Corrosion results and an understanding of corrosion mechanisms for volcanic and acidic well fluids provide a materials performance database for the anticipated deep well fluids. This growing materials database is being integrated with the results of thermodynamic modeling of the corrosion chemistry in acidic wells to develop predictive materials performance models.

This paper reviews the current status of the database of corrosion results and predictive corrosion models. The database of evaluated and interpreted results has provided guidelines for materials selection and corrosion control options for aggressive deep and acidic well fluids.

1. INTRODUCTION

The IEA research collaboration program on deep geothermal developments was formally started in March 1997. The objective of the program, which is divided into three subtasks is to address the issues necessary for the commercial development of deep geothermal resources at a depth of 3000 m and deeper (Uchida and Kimbara, 1996). The work plan proposed: (1) promotion of information exchange through joint research and workshops, and (2) creation of a database through which the participating countries could share information related to geothermal resources. Three Subtasks are currently active: A- Exploration Technology and Reservoir Engineering, B- Drilling and Logging Technologies and C-Materials.

This paper reviews work activities of the Subtask C-Materials dealing with fluid chemistry and corrosion in aggressive fluids, and provides guidelines for materials selection and corrosion control for deep and acidic geothermal resources developments.

2. OUTLINE OF SUBTASK-C ACTIVITIES

In the four year work program for Subtask C-Materials two types of activities were conducted. The first was to gather information on past and present experiences, corrosion tests and research on materials in deep and acidic geothermal systems. The second was to perform corrosion tests of materials in field trials and laboratory tests as were required to help in the materials selection process and corrosion mechanism investigations. The tests were conducted in wellhead environments, production boreholes, and in natural volcanic fumaroles and hot spring environments. The tests also included simulations of two-phase acidic flow and pressure vessel laboratory testing of materials in acidic fluids.

Three principle participant organisations and their research;

- High temperature corrosion and utilization of deep geothermal energy system by Materials Performance Technologies, New Zealand
- Materials for geothermal energy utilization by Tohoku National Industrial Research Institute, Japan
- Investigation of corrosion of casings and pipelines of geothermal plants by NEDO, Japan

Information exchange through visits to organizations;
At the end of 1996, prior to the formal IEA initiative, the Japan and New Zealand participants sent an open letter to a number of companies and research institutes concerned with geothermal materials selection. The letter solicited materials test results and experience in deep and acidic geothermal environments.

Responses were received from seven countries including Indonesia, Italy, Japan, Mexico, New Zealand, Philippines and USA. The collected data on materials, fluid chemistry and corrosion in aggressive and deep geothermal wells was presented at a NEDO International Geothermal Symposium in 1997 (Sanada, et al., 1997).

The Japan and New Zealand participants visited a number of organizations to exchange information on the materials and chemistries. These visits with other researchers and developers resulted in informal participation in the research program from companies in Japan, The Philippines and USA. This new awareness stimulated additional collaboration and publication of relevant research results (ie Gallup and Parison, 1998).

Compiled references;
A compilation of published literature references on corrosion chemistries, materials test results and experiences in acidic and deep geothermal environments was prepared. Over 160 papers were collected from “Geothermics”, “GRC Transactions”, “Geochemical Journal”, “New Zealand and Philippines

Geothermal Workshop and Conference Proceedings", "Journal of the Japan Geothermal Energy Association, and other corrosion journals. The literature database, which provides the title, author(s) and abstract in English for each article is available through the www system. Chemistry data for deep and acidic wells was separately tabulated (Sanada and Lichti, 1997).

Corrosion modelling;

Corrosion models were developed for downhole and wellhead environments under flowing conditions. These models include the corrosion chemistry and mineral corrosion product phase stability as well as the effect of fluid velocity on erosion corrosion. The models help to predict materials performance problems and to identify corrosion control options. Chemistry models were integrated with materials performance results obtained from acid wells in Japan and The Philippines, acidic wellhead applications in the USA and acidic volcanic hot spring environments in New Zealand. Many of the available results have been presented in international meetings; NEDO International Geothermal Symposium 1997, GRC 1997, PNOC-EDC Geothermal Conference 1998, New Zealand Workshop 1997 and 1998.

3. MODELING OF CORROSION PROCESSES

3.1 Corrosion in Wellhead Fluids Under Flowing Conditions

Figure 1 is a schematic illustration of material corrosion rates as a function of fluid velocity. Corrosion rates increase abruptly as the fluid velocity approaches around 100m/s. Curve A represents a corrosion rate of carbon and low-alloy steels in acidic fluid flow, for example at pH 3 without dissolved oxygen. Initially the corrosion rate increases with flow velocity in the range up to around 1m/s, where the corrosion rate is as much as 10 times greater than that at lower flow rates. This increase in corrosion rate is followed by a plateau in the rate as the fluid velocity is increased up to around 100 m/s. Above this flow rate the corrosion rate increases to unacceptable levels.

Curve B represents a corrosion rate in an alkaline or neutral pH fluid flow with dissolved oxygen. The curve has a peak within the velocity range of 1m/s, after which corrosion rate is again low and acceptable up to the high velocity range of 100 m/s. Curve C represents corrosion rate of stainless steels in acidic fluids with a pH of about 3 as a function of flow rate.

It is considered that the two-phase fluid velocity of geothermal fluid in operation should be kept less than 100m/s.

Corrosion in acidic two-phase fluid flow

Figure 2 shows materials performance obtained in corrosion tests in two-phase flows from an acidic production well, of which the chemistry is shown in Table 1 (Sanada et al., 1995). The corrosion rates are plotted as a function of temperature in the range of 105 to 137ºC for various values of pH.

The corrosion rate results show a strong dependence on alloy content at pH 4.5, especially for low allow steels, and the dependence decrease, as the pH decreases to 2.6. At pH 2.6 the low alloy steels all have a similar high corrosion rate while the high alloy materials begin to show a strong dependence on alloy content. At pH 2 only Hastelloy C-276 and the Titanium alloy show low, acceptable corrosion rates.

Figure 3 gives a comparison of corrosion in flowing fluids vs that in static fluids. The Figure shows the effect of turbulence on corrosion rate at 137ºC. Corrosion of all materials was independent of the flow turbulence in pH 4.5 solution. In pH 3.2 and pH 2 solutions, the corrosion was significantly increased in the more turbulent fluids. Again, only Hastelloy C-276 and the Titanium alloy gave acceptable corrosion rate results at pH 2.

3.2 Corrosion In Wellbore Environments

Simulation of wellbore chemistry

Thermodynamic models can be used to calculate the chemistry of the inflow into deep wells from the measured surface chemistry and enthalpy. This information together with wellbore simulation allows the calculation of chemical conditions throughout the wellbore (Lichti et al, 1998).

Figure 4 illustrates results for a well in The Philippines having as analysed wellhead chemistry shown in Table 2 and a flowrate of 120 kg/s. The obtained results suggest a variation in corrosion chemistry as the fluids rise in the well. Water pH decreases and total active S increases as the fluid raises up the well.

Potential-pH models

The calculated wellbore chemistry can be used to model the tendency to formation of passivate films on carbon steel bore casing material using potential-pH Pourbaix diagrams. Figures 5(a) and (b) were prepared for the conditions defined in Figure 4 for the Fe-S-H_2O system at 300 and 150°C and show corrosion product stability as functions of temperature of the produced fluid and water chemistry (Lichti et al., 1998)

Figure 5(a) representing reservoir conditions at 300°C suggests formation of iron sulfide films, which have been shown under lower temperature conditions to provide protection to the underlying steel and acceptably low corrosion rates. The estimated pH and corrosion potential ranges are well within the stability areas for the formation of protective iron-sulfide corrosion products.

The chemical model predicts that at lower temperatures the concentration of S species in the water phase is decreased by boiling and the resultant phase separation. The effect on phase stability of the iron sulfide corrosion products is not dramatic in comparison with the diagram for 300°C, compare Figures 5(a) and 5(b). The decrease in temperature as the two-phase fluid moves up the well gives little change in the stability areas of the iron sulfides. However, the continuing decrease in pH moves the corrosion reaction area below the lower pH limit for FeS and into the region of Fe^{++}, where free corrosion is predicted.

3.3 Corrosion in natural volcanic fluid

The corrosion chemistry of fluids encountered in natural volcanic fumarole and hot spring environments is determined by the presence of corrosive species such as SO_2, H_2S, HCl, HF in the fumarolic gases and SO_4^{2-}, Cl^-, F^- in the hot springs. These same corrosive species are expected in deep and acidic geothermal reservoirs and in magma-ambient geothermal environments. Corrosion tests of materials exposed in such volcanic environments were undertaken to give an indication of relative materials performance in aggressive fluids.

White Island , New Zealand was chosen for exposure trials because of the relative ease of access to moderate temperature fumaroles and near boiling hot springs.

Corrosion in volcanic gases

A superheated steam fumarole (200°C), Noisy Nellie (WI #9) was used to study the corrosion of a range of alloys. The fumarole was aerated as indicated in Table 3. Figure 6 shows corrosion rate results for a range of corrosion resistant alloys plotted versus the molybdenum content. The corrosion rates were very small or negligible for the alloys containing more than 8%Mo. The rates for the duplex stainless steels, the high-alloy stainless steels and the nickel-base alloys increased linearly with decreasing Mo content in the range less than 8%. Molybdenum appeared to play a key role in enhancing resistance to corrosion in this aerated environment.

In other volcanic trials, notably in dry gas non-aerated (superheated) environments, corrosion rates for all alloys tested were very low due to passive film formation (Lichti et al 1996). In non-aerated fumarole gas environments alloys containing about 6% Mo, gave acceptable performance; 0.26mm/y for alloy 1925 with 6% Mo, 0.15 mm/y for alloy G3 with 7%Mo (Davison and Redmond, 1988).

Figures 7(a) and (b) are phase stability diagrams for Fe and Mo and their reaction compounds as a function of log pSO_2 vs log pO_2. Figure 7(a) shows the air-free gas mixtures have partial pressures which stabilise layers of Pyrite (FeS_2) and Troilite (FeS) or Pyrrohotite ($Fe_{1-x}S$) as the initial surface is approached from the iron sulfide/gas interface. This gives a reason for the good performance in non-aerated gaseous environments. The addition of air stabilizes non-protective sulfate species and this gives an explanation for the high corrosion rates. Figure 7(b) indicates that formation of protective Mo oxides is independent of pO_2.

Corrosion in volcanic hot springs

The corrosion chemistry of hot pools on White Island, Black Pot and Hot Pool #13a is summarized in Table 4. The corrosion rates in Black Pot (pH 4.5) were similar to or greater than those obtained in static autoclave tests at pH 3. The corrosion rates in Hot Pool #13a (pH 1) were similar to or greater than those observed in static autoclave test at pH 1 (Lichti et al., 1997a).

4. CORROSION CONTROL AND MATERIALS SLECTION

Materials commonly used for bore casing and wellhead equipment of geothermal wells are readily corroded in acidic fluids containing excess Cl (from HCl gas) and SO_4. The corrosion rate is accelerated at the wellhead and the upper well sections where the flow turbulence is increased and the pH is decreased. Two approaches to the selection of process and plant for these locations are available (Lichti and Sanada, 1997):

- To use more resistant alloys for wellhead equipment and the bore casings, together with small sized separation or heat exchange plant close to the wellhead and immediate treatment and reinjection of the spent fluid.
- To control downhole corrosion by dilution, pH adjustment or inhibition of the acidic fluids to permit the use of carbon steels, or the least expensive stainless.

4.1 Guidelines of Corrosion Control and Materials Selection

Geothermal fluids having a pH greater than 4.5 have been successfully produced using carbon and low alloy. Fluids having pH lower than 4.5 have not been successfully produced in wells cased with carbon and low alloy steels. Many of these wells have been developed for reinjection or cemented shut for safety reasons (Sanada et al., 1997). Aggressive high-salinity brines at Salton Sea, USA have been developed for production using sacrificial cement-lined casings for the bore casings and surface piping (Pye et al., 1989, Moeller and Cron, 1997). Titanium alloys are used for long term production of the brines.

These experiences and the discussion in the previous sections lead to proposed guidelines for corrosion control and materials selection for deep and acidic wells as shown in Figure 8:

- In near neutral to alkaline pH fluids having pH greater than 4.5, carbon and low alloy steels appear to be suitable for bore casings.
- In acidic fluids with sulfate rich waters containing low levels of chloride salts, carbon and low alloy steels are readily corroded at pH less than 4.5. In deep high temperature environments where the level of total free S is high the corrosion chemistry may be such that passive films are formed and carbon and low alloy steels give satisfactory performance. Chemical modelling can be used to determine if these conditions exist. These fluids having sulfate controlled acidity become more aggressive as the fluids rise in the well and at shallow depths high alloy materials such as duplex ferric-austenitic stainless steels or other corrosion resistant alloys are required for bore casings. Application of pH adjustment and/or inhibitors for well bore corrosion control has been advocated for pH values as low as 3.
- Lower pH solutions (less than 3) will require new technologies.
- In hyper-saline brines the successful use of a high alloy Ni-base alloys and Titanium alloys has been demonstrated. Temporary downhole production can achieved using sacrificial cement-lined production tubing, which is also suitable for surface piping.
- In superheated steam geothermal production systems with a high concentration of HCl gas generally require some form of pH adjustment after the point where acidic condensate first forms in the upper well sections, wellhead equipment and surface pipelines.
- Upper well sections, wellhead and pipelines may also experience excess turbulence which accelerates corrosion in aggressive acidic environments. In these instances careful plant design is required to keep flow rates low for the materials selected.

5. CONCLUSIONS

The IEA Deep Geothermal Resources Iniative Subtask C on Materials has been progressed by surveys of deep geothermal well experience and research results. The work activities under the task program have encouraged information exchange and research collaboration with those who are concerned with materials for deep and acidic well fluid applications:

- Chemistry data and materials experience were compiled from published literature to develop a database of materials performance in deep and acidic geothermal fluids.
- Corrosion models were developed for downhole and wellhead environments under flowing conditions to model the effect of fluid velocity on corrosion, the corrosion chemistry and mineral corrosion product phase stability.
- Corrosion performance of materials was examined in volcanic environments, where the presence of corrosive species might be similar to that in deep wells and magma-ambient situations.
- Guidelines of corrosion control and materials selection were proposed for deep and acidic geothermal wells.

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Table 1. Production chemistry used for corrosion tests in an acidic two-phase flow (Sanada et al., 1995).

T	pH	Li	Na	K	Ca	Mg	Cl	SO_4	B	SiO_2	NH_3	HCO_3(t)	H_2S(t)	Fe	Al
℃	(25C)	mg / kg													
158	3.2	—	1733	—	580	149	4630	33	—	92	—	—	—	167	—

Table 2. Production chemistry used for simulation of wellbore chemistry (Parrilla et al., 1997).

H	SP	CO_2	H_2S	NH_3	He	H_2	Ar	N_2	CH_4
kJ/kg	Mpa(a)	mmoles/100 moles steam							
1287	0.480	400	24.3	0.24	n.a.	0.0878	0.051	12.667	0.954

pH	Na	K	Ca	Mg	Fe	Cl	F	SO_4(t)	NH_3(t)	SIO_2
25℃	mg/kg									
3.1	3117	950	82	25	282	6175	3.1	508	15.6	910

Table 3. Geochemistry of fumarole environments used for corrosion Test (Lichti et al., 1997)

Location	Date	T	CO_2	H_2S	SO_4	NH_3	HF	HCl	CO	H_2	O_2	N_2	CH_4	Ar	H_2O	Gas
		℃	mmol gas / 100 mol steam													wt%
Noisy Nellie WI#9	21.2.95	193	1381	94.3	133	15.5	3.87	35.1	—	43.1	(62.8)	119	5.48	0.90	98169	4.3

Table 4. Geochemistry of hot pool environments used for corrosion tests (Lichti et al, 1996) .

Lacation	T	pH	Li	Na	K	Ca	Mg	Cl	SO_4	B	SiO_2	NH_3	HCO_3(t)	H_2S(t)	Fe	Al
	℃	(25C)	mg / kg													
Black Pot	93	5.07	0.26	270	49	188	157	619	1044	0.68	327	102	—	0.07	14.5	6.5
Pool #13a	99	1.03	0.34	105	51	394	228	3474	12040	0.97	456	0.81	—	—	782	103

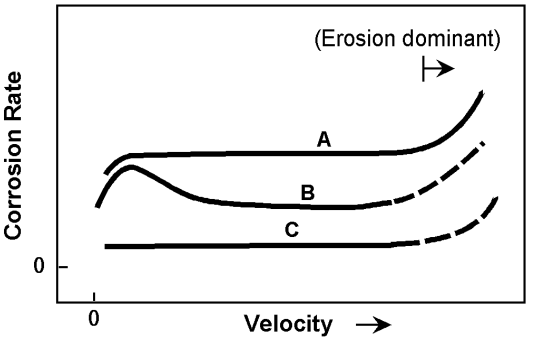


Figure1. Schematic digagram showing typical features of materials corrosion rate in flowing fluids at different velocities.

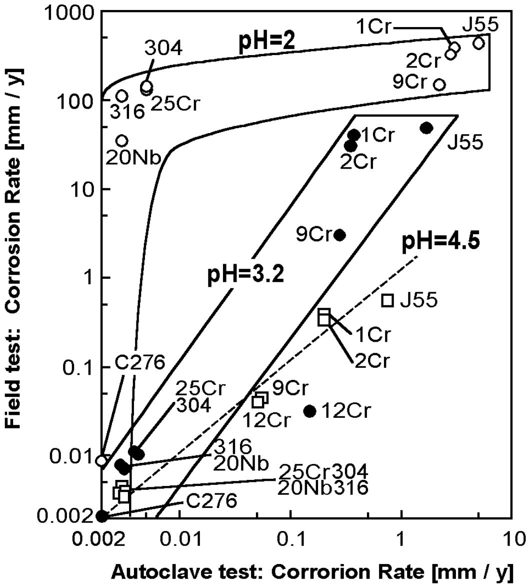


Figure 3. Comparison of corrosion rates in flowing two-phase fluid tests with static autoclave tests. Temperature: 137°C, velocity in field test: 70 - 100 m/s. ○: pH2, ●: pH3.2, □: pH4.5. (Sanada et al., 1998)

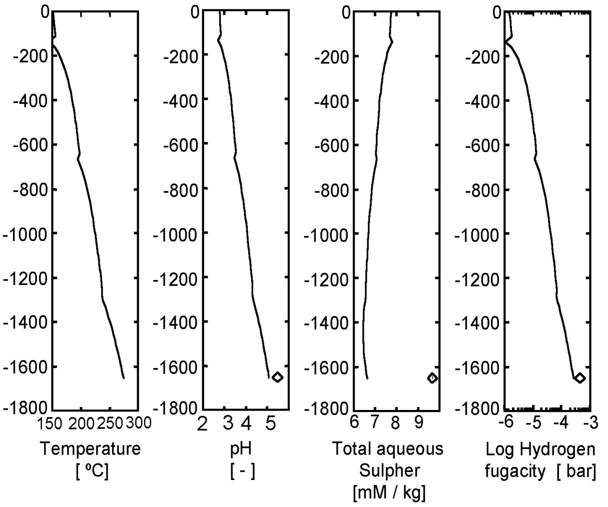


Figure 4. Results of wellbore chemistry modelling (Lichti et al., 1998).
◇ : values for liquid water at 300°C.

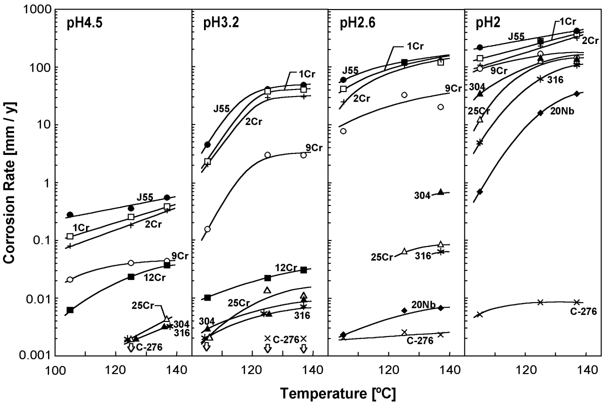
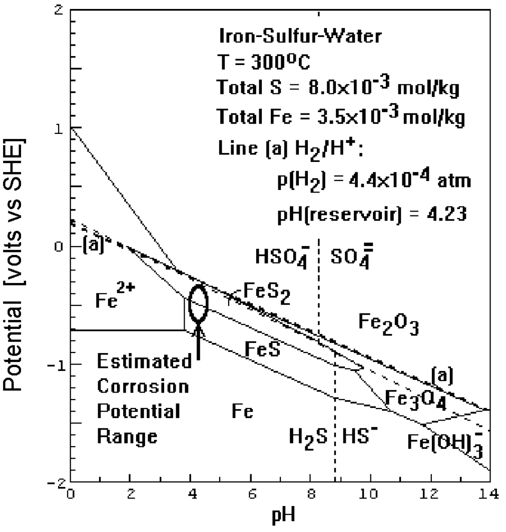
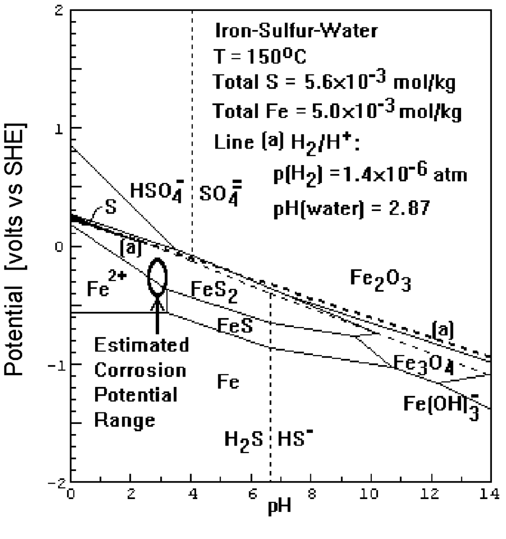


Figure 2. Effect of temperature on corrosion rate in two-phase fluid test. v: 70~100m/s, Quality: 0.4~0.6 (Sanada et al., 1998).



(a) Single Phase Reservoir Entry at 300°C.



(b) Produced Wellbore Water Phase at 150°C.

Figure 5. Potential-pH pourbaix diagram for an acidic wellbore chemistry (Lichti et al., 1998).

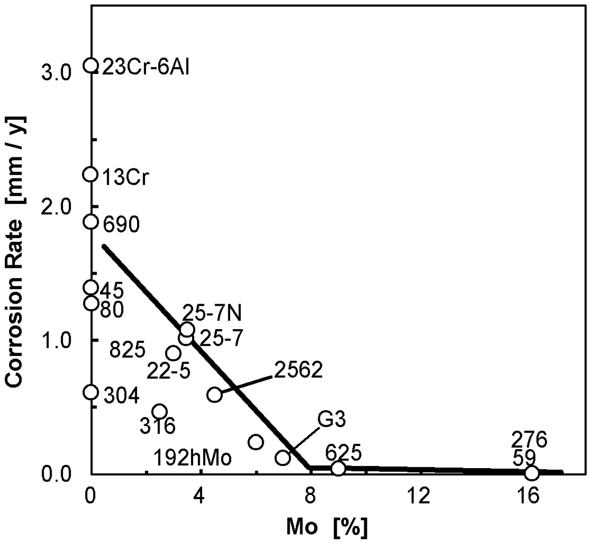
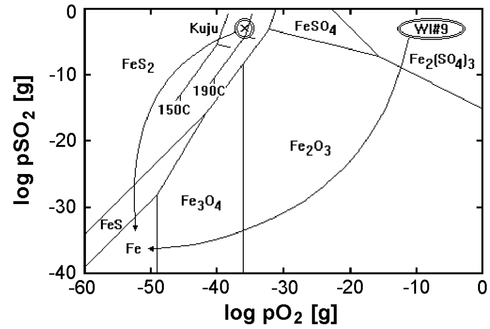
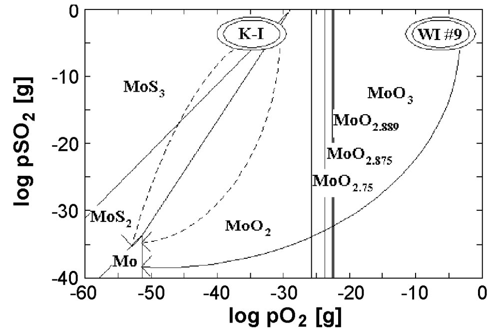


Figure 6. Effect of molybdenum content on the corrosion rate (Kurata et al., 1995).



(a) Phase Stability Diagram for Fe-SO_2-O_2



(b) Phase Stability Diagram for Mo-SO -O

Figure 7. Phase stability diagrams for Fe, Mo in volcanic gases at 230°C. Arrows indicate possible reaction paths (Lichti et al., 1997).

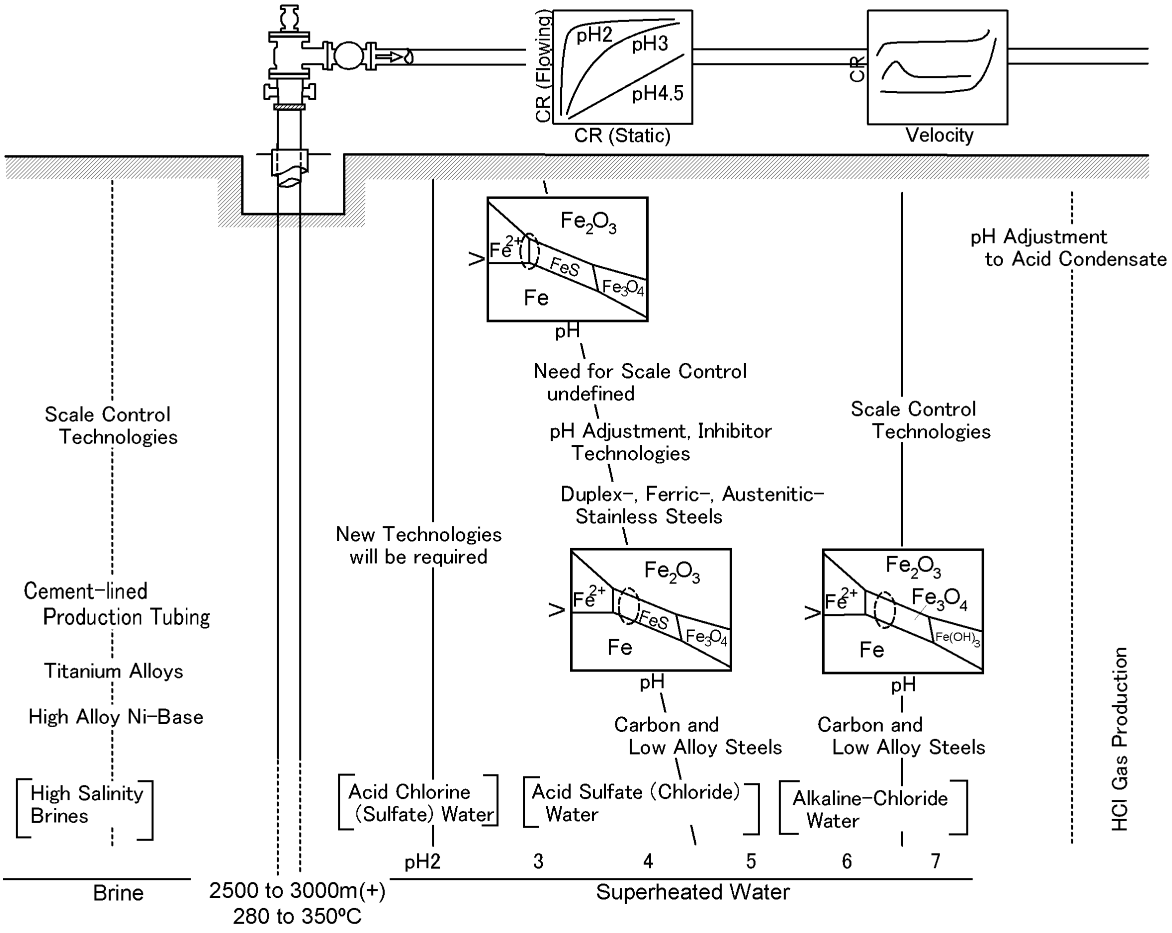


Figure 8. Guidelines of corrosion control and materials selection for deep and acidic geothermal wells.