

PROSPECTS FOR THE EVALUATION AND DEVELOPMENT OF MATERIALS UNDER IEA RESEARCH COLLABORATION PROGRAM ON DEEP GEOTHERMAL RESOURCES

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ABSTRACT

Deep-seated geothermal reservoirs (>3000 m) have been identified as a viable source of energy within existing and new geothermal fields. Drilling and proposals for utilization of these resources is increasing. The discharge water and steam chemistries of deep-seated geothermal production wells are expected to contain significant concentrations of aggressive species CO₂, H₂S and HCl for example and may be of high salinity (high Cl) and low pH (high SO₄). The corrosion properties of these fluids have not been fully defined and there is a need to collect and evaluate materials results and experience relevant to the selection of materials for deep-seated geothermal developments. The IEA research program was proposed to encourage information exchange and collaborative research activities including materials research. A four year program of activities is outlined to progress this area of research.

INTRODUCTION

Deep geothermal resources, which are tentatively defined as those at a depth of more than 3000 m below the ground surface, have the potential to provide considerably more energy than shallow reservoirs. A number of countries have begun to drill deep geothermal wells and some of these activities are reported in this symposium. In Japan for example the New Energy and Industrial Technology Development Organization (NEDO) drilled a deep well, which reached 3729 m depth in the Kakkonda geothermal field. A total of eight wells greater than 4000 m in depth have been drilled in Mexico at a number of fields including Cerro Prieto. Many other countries have drilled or plan to drill deep wells.

Materials used in exploration, drilling and well completion depend critically on the properties of the encountered and produced fluids, in particular on their corrosive effects, so the corrosion chemistries have to be sufficiently well understood to facilitate prediction of corrosion performance and selection of reliable materials. In deep geothermal systems fluids from the reservoirs might be expected to result in more corrosion of conventional construction materials because of higher temperatures and lower pH values.

This paper reviews experiences concerning materials for deep geothermal developments, the fluid chemistry and the corrosion in aggressive fluids and describes the IEA research collaboration program on the materials for deep geothermal developments, which is expected to start in March, 1997.

DEEP WELL DEVELOPMENTS

1. Indonesia

A geothermal field in Indonesia drilled to depths of more than 2000m gave temperatures higher than 320°C. The wells encountered corrosive fluids having pH value 1 and temperatures of 200°C, at 600 m depths which destroyed both cement and casing. A project has been initiated to study cement and casing for corrosive and high temperature fluids in acidic geothermal fluids (Sudarman, 1996).

2. Italy

In the last decade a number of deep geothermal exploration wells have been drilled. In the well "Carboli 11" having a total depth of 3455 m in the Larderello geothermal field, a temperature of 427°C was measured at a depth of 3328 m. Fluid inclusion and hydrothermal mineral analysis indicated a high salinity (~ 32 wt% NaCl equiv.) brine of magmatic derivation at 3445 m depth (Giovanni, 1995).

3. Japan

By the year of 1993 the total number of deep geothermal wells, which were more than 2440 m in depth and of which the deepest one was on the order of 3200 m in depth, was twenty-four (Yagi et al., 1994, Saito, 1994). Maximum temperatures of the produced fluids were 373°C in a bore hole in the Fushime geothermal field, and 412°C in a bore hole in the Kakkonda geothermal field.

In 1992 the New Energy and Industrial Technology Development Organization (NEDO) started to investigate characteristic of deep geothermal systems under a project entitled 'Deep-seated Geothermal Resources Survey' and to drill a deep well in the Kakkonda geothermal field in Japan (Sasada et al., 1993). The deep well was named as WD-1A, which reached 3729 m depth in 1995, but did not encounter steam production zones (Yagi et al., 1995, Saito et al., 1996). The well is the deepest of the geothermal bore holes in Japan. In the well completion 13 3/8" casing L-80, 61&68 lb/ft and 9 5/8" casing L-80, 47 lb/ft were used, and the cementing jobs for both casings were performed using three and two-stage cementing methods, respectively.

Temperature measurements near the bottom of the well were made using temperature indicators of metallic fusion compound tablets and pure metal tablets (Ikeuchi et al., 1996, Sasada et al., 1996). The temperature was found to be over 500°C at 3700 m depth in the bore hole in the heat conduction zone, which was below 3100 m. The temperature of over 500 °C is again the highest of the geothermal bore holes in Japan. They also sampled supersaline and metal rich brine from the well bottom and confirmed that the borehole fluid contained magmatic substances. The work on this well site is continuing.

Materials research on the corrosive effects of HCl containing two-phase fluids encountered in production wells has been conducted over a number of years in Japan. (Kurata et al, 1995, Sanada et al, 1995). Suitable cost effective materials for production tubing have been successfully trialed for deep geothermal wells of pH>3, for example Alloy 22Cr-5Ni.

Work on corrosion in volcanic environments having aggressive gas chemistry was initiated in Japan in 1992 at Kuju-Iwoyama (Saito et al, 1994).

4. Mexico

There have been some experiences in deep geothermal drilling in places like Cerro Prieto (Puente, 1996). They have drilled eight geothermal wells with more than 4000 m depth (4325 m is the deepest one) and found temperatures up to 360°C. These wells were completed using conventional casing designs, for example 9 5/8" casing C-75, 45 lb/ft, Hydrill 563, and slotted liner 4 1/2" C-75, 29 lb/ft, Hydrill S.E.U.

5. New Zealand

Deep drilling is considered to be a viable option for extending the production capabilities in existing geothermal fields of Ohaaki and Wairakei. Deep drilling in search of additional steam at Ohaaki has been tried and is reported separately in this symposium. The wells were shallower than planned and produced fluids were similar to those of the shallower fluids.

A joint Japan/New Zealand initiative began to characterise the corrosion properties of a range of engineering alloys exposed to natural volcanic environments on White Island, New Zealand in 1993 (Kurata et al, 1994, Kurata et al, 1995, Lichti et al, 1996). The results are providing indications of alloy types which might be suitable for use in high temperature, acidic deep-seated geothermal fluids.

A second New Zealand/Japan collaborative project on "Utilisation of Deep Geothermal Resources" was

initiated in 1996 with the aim of defining the corrosion chemistry of typical deep-seated geothermal production fluids and to explore energy process and plant options. It is planned to simulate aggressive environments, where materials selection criteria are unclear, in the laboratory, for testing of corrosion resistant alloys.

6. USA

Brookhaven National Laboratory (BNL) is performing work on two topics that are applicable to deep geothermal resources development (Kukacka, 1996). The first is to develop advanced materials systems for use in the completion of high temperature (300-500°C), low pH geothermal wells. As part of this work they have synthesized and laboratory tested a CO₂-resistant, lightweight, cementing material that meets the following criteria: 1) carbonation rate <5% after 1 yr in brine at 300°C containing 500 ppm CO₂, 2) slurry density < 1.2g/cc, 3) compressive strength >5 MPa at 24 hr age, 4) bond strength to steel well casing >0.07 MPa, 5) pumpability of approximately 4 hr at >100°C, and 6) H₂O permeability < 0.1 m Darcy. The cement is a non-portland cement-based material containing Na₂O, CaO, Al₂O₃, SiO₂, P₂O₅ and H₂O. Testing in a chemically harsh geothermal environment will take place in the Summer of 1997 when the cement is used in a well completion.

A second topic under investigation is advanced materials for the control of lost circulation episodes. Prior to pumping cement for a lost circulation treatment the bit is invariably removed from the drillstring, requiring a round trip on the drill pipe that takes about 1 hour for each 300 m of hole depth. The bit is removed because of the fear of plugging a bit nozzle and having the cement set up inside the drill pipe. If it could be guaranteed, however, that the cement would not set up in the drill pipe for a significant length of time, the cement could be pumped through the bit nozzles with less trepidation. By not removing (then replacing) the drill bit, two hours of rig time would be saved for every 300m of hole depth. For a typical 1000 m loss-zone depth, this amounts to 6 hours per loss zone.

Under this project, they are attempting to develop and test a cement with an encapsulated accelerator that does not react to set the cement until the encapsulant is somehow ruptured. This could be accomplished when the cement either passes through the bit nozzles and the encapsulant is sheared off the accelerator, or the cement flows into a loss-zone fracture and heats to a temperature that melts the encapsulant. Rapid, controllable setting or thickening once the cement is outside the drill pipe would significantly improve the sealing capability of the cement.

7. Philippines

Shallow wells in the Philippines have on occasion encountered aggressive acidic fluids (Maturgo, 1996). These wells have been too corrosive to use for production but have been successfully used for reinjection. Research on the geochemistry has concentrated on developing an understanding of the origin of these fluids. Some research on materials has been done but the wells have not been further developed for production and the majority of the acid wells have been cemented shut (Ferrer, 1996).

CHEMISTRY OF DEEP GEOTHERMAL FLUIDS

According to theories on chemical substance transportation to deep geothermal fluid, chemical substances could be supplied into deep geothermal fluid through the following three processes (Noda, 1992):

- (1) differentiation of magmatic emanation,
- (2) NaCl vaporization under high-temperature, high-pressure condition,
- (3) chemical substance leaching from rock.

Actual geothermal fluids might contain chemical substances which are supplied through a combination of these three, and the fluid characteristics are largely influenced by volcanic activities and geological environment. From a corrosion point of view, therefore, it must be considered how much aggressive substances such as HCl, H₂S, SO₂, HF as well as NaCl are contained in the fluids.

It is generally considered that the discharge fluid chemistry of deep geothermal wells will be more aggressive than conventional geothermal, however little data is available for deep wells. Many shallow wells have produced acidic fluids which are considered to show characteristics of deeper reservoir fluids. Tables 1 and 2 show the discharge water chemistry of acidic fluids in geothermal wells which have been drilled in Japan and Philippines, respectively. The results shown, although not for deep geothermal wells do give some indication of the more aggressive chemistries anticipated in deep-seated geothermal developments.

Table 1. Discharge Water Chemistry of Acid Fluids in Geothermal Wells in Japan (NEDO-P9211, 1992).

Well	Depth (m)	Tmax	pH		Composition (mg/l)													
		(°C)	Water	Steam	Na	K	Ca	Mg	Cl	SO ₄	B	SiO ₂	NH ₃	HCO ₃	H ₂ S	Fe	Al	
A-2	1507	280	3.6-49		275	46.6	22.9	2.4		854-1400		759			0.1	759		
A-2	945	250	3.3	5.6	956	318	90	34	18	3643		1312			7.3	496		
A-2	558		3.9		383	41.4	18.3	2.3	4.9	870		422			0.6	12.8		
A-2	1207	250	3.9	5.78	134	53.5	56.3	2.9	5.5	894		376			1	114		
A-3	2465	330	3.5		1090	242	2.7	0.4	1880	116		1680				22.9	0.12	
A-3	2818	320	3.99	4.5	757	172	196.6	0.6	1400	63.2		1490				21.2	0.99	
A-3	3000	333	4.7-5.1		475	105	1.78		732	63.4		1470						
B-1	850	198.7	2.4-2.9				20.5	26.3	449.5	658.7						38.1		
B-1	1067	210.7	3.6-5.9		390	64	12	14.1	597.4	378.6						23.9		
B-1	1200	202.7	3.1-3.9				15.8	11	502.6	447.1						52.5		
B-2	1065	250	2.8-3.3	4.96	308	84	13.63	60.2	239.6	1308		528				307		
C-1	1350	238	3.3	4	1788	503.5	408.4	137	5286	55.2		510				323	3.83	
C-1	1300	238	2.6	4.4	3120	810	1460	270	9570	201		144				648		
C-1	375	184	3.3	4.4	1950	439	408	48.4	5630	31		515				220	4.32	
C-1	1500	261.3	3.4	4.1	1900	440	450	33	4910	19		690				150	0.53	
C-1	1000	224.9	3.4	4.2	1400	360	470	34	480	19		660				110	0.22	
G-1	2152	242	8.8-3.5	4	567	70.6	11.6	0.36	764	325		551				31.1	0.82	
G-1	2182	243	3.4	4.2	503	56.3	15.7	1.91	612	360		452				40.4	0.97	
H-1	1506	326-360	4.7	3.8	13200	3450	1320	23	3E+05	31		1070				1.6		
H-1	2050		3.9	4.3	17400	4700	1650		32700			1250				120		
H-1	2505		4.7	4.2	14800	4190	1850	8	31500	36		853				25	0.27	
H-1	2045		4.7	4.5	15800	4970	1780	2.7	31800	35		1180				10	0.3	
H-1	1701		3.8	3.2	14900	4710	1540	17	29400	36		1210				84	0.35	
H-1	2139			4.4	4.2	13800	4570	1330	12	1200	55		1210				54	0.08
I-1	1801	294.3	2.7	4.2	880	250	4.4		1180	440		1080			3			
I-1	1267	240.5	2.82	4.8	818	190	8.1	2	980	364		1000			0.5	26	0.47	
I-1	1198	263.8	2.4	5	765	167	17.4	4.8	7600	697		1036				39.7	0.09	
N-59-SK-6	1700	228.6	4.4-5.9	4	4500	570	98	110	255	320		25			5.1	170		

Table 2. Representative Discharge Water Chemistry of Acid Fluids in Geothermal Wells (Maturgo, 1996).

Location	Type	Tmax	Chemical Composition (mg/kg)													
		(°C)	pH	Na	K	Ca	Mg	Cl	SO ₄	B	SiO ₂	NH ₃	HCO ₃	H ₂ S	Fe	Al
CN-2KD	low Cl	250	4.83	455	46	17	8.2	206	871		638				4.25	
LG-1D	high SO ₄	240	3.95	580	190	8	2.7	769	860		951				145	
MG-90	high Cl (Cl>Na+K)	305	3.11	4283	1200	115	21	7940	74		1128				77	
MG-15D		280	3.66	3080	747	60	12	5663	136		1000				31	
AP-7D		320	2.08	840	130	33	24	2058	347		871				469	
PIN-2D		330	2.26	2850	516	69	223	4474	2491		1233				780	
PIN-3D		330	2.55	17400	3540	2202	133	37760	500		1660				525	
KN-2D		300	4.25	5780	1103	64	2	9625	597		978				9	
KN-3		320	4.85	5573	1554	163	0.51	10741	192		1145				0.87	
BL-1D		310	4.91	1660	384	8	0.15	2922	410		1018					
PN-22D		295	3.75	3020	680	24	3.28	5316	258		1148					
KN-1D	high Cl	300	2.4	3786	865	10	10	6638	1125		1136				121	
CN-2D	high SO ₄	240	3.79	2910	275	7	9	4272	1635		592				189	
LB-1D	(Na+K>Cl)	279	3.48	4527	643	37	119	7517	1089		1105				145	
LB-3D		264	3.46	3975	520	7	23	6713	975		837				7	
LB-5D		254	3.04	3738	523	2	183	5877	2036		863				233	
PIN-1		264	4.1	6070	608	98	162	10104	1309		555				86	

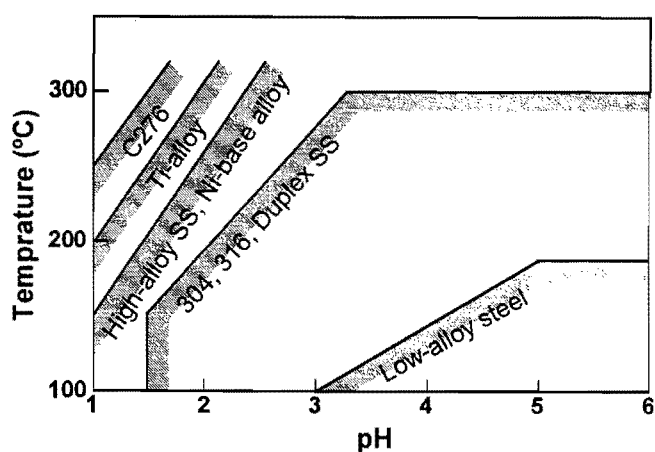


Figure 1. Schematic temperature - pH diagram showing regions of acceptable performance for materials exposed in static autoclaves (Sanada et al., 1995).

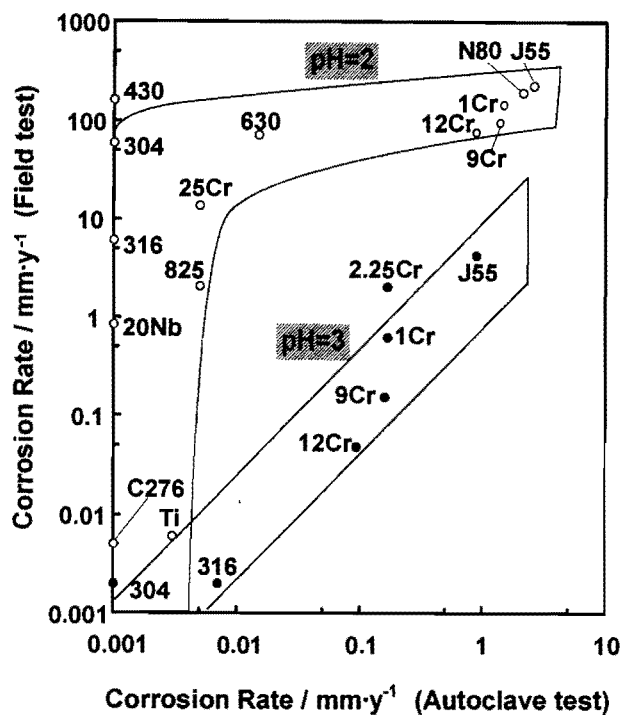


Figure 2. Comparison of corrosion rates in the flowing two-phase fluid tests with the static autoclave tests. Test conditions: temperature of about 100°C, pH values of 2 and 3, flow velocity in the field test of 70 to 100 m/s (Sanada et al., 1995).

CORROSION OF ENGINEERING ALLOYS IN AGGRESSIVE FLUIDS

Reviews on materials performance in a range of geothermal fluids, which aimed to provide some guidelines for selecting materials, have been published (DeBerry et al, 1978, Ellis et al., 1981). Corrosion of engineering materials has been experienced on pipelines, well casing, drilling tools and well logging tools in conventional geothermal systems. These were due to fluids containing CO₂, H₂S and other gases as well as H⁺, Cl⁻ and other corrosive sulphur species.

Deep geothermal resource developments might be expected to be more corrosive because of higher temperatures and higher concentrations of corrosive substances transported through the above mentioned three processes (Noda, 1992). Conventional carbon and low-alloy steels and stainless steels, which have been used in shallow geothermal developments in many cases, must be assessed for their corrosion resistance before they are used in the deep-seated well fluids. Other alloys having greater corrosion resistance might be required in applications where corrosion rates of the conventional materials are high.

Engineering alloys have been examined under acidic (HCl) conditions in laboratory tests and field tests. Table 3 shows an example of the alloys tested in acidic fluids (Sanada, 1995). Figure 1 is a schematic diagram derived from the test results. This figure gives guidelines for selection of alloys at high temperatures in acidic fluids at static conditions. Figure 2 shows the relation between results of the field tests conducted at velocities 70 to 100 m/s and results of the static autoclave tests. This figure summarises corrosion data used for selection of materials in high velocity acidic fluids.

Table 3. Metals and alloys tested for resistance to corrosion in acidic fluids (Sanada et a., 1995).

Material Type	UNS Number	Normal Composition
Carbon and Low Alloy Steels		
SS400	---	Carbon steel, tensile strength 400MPa
Corten	---	Atmospheric corrosion resisting steel
N80	---	API standard
L80	---	API standard
Martensitic Stainless Steel		
13Cr		S41000 Yield strength 560MPa
Ferritic Stainless Steel		
23Cr-6Al	---	23Cr-6Al
Austenitic Stainless Steels		
SUS304	S30400	Standard alloy, 18Cr-8Ni
SUS316	S31600	Standard alloy, 18Cr-10Ni-2.5Mo
Duplex Stainless Steels		
22Cr-5Ni	S31803	22Cr-5Ni-3.0Mo-0.15N
5Cr-7Ni	S32750	25Cr-7Ni-3.5Mo-0.10N
25Cr-7Ni-N	S32750	25Cr-7Ni-3.5Mo-0.20N
High Alloy Stainless Steels and Nickel Alloys		
SS 2562	NO8904	19.5Cr-25Ni-4.5Mo-1.5Cu
1925hMo	NO8926	21.5Cr-25Ni-6Mo-1Cu
Alloy 625	NO6625	21.5Cr-61Ni-9Mo-2.5Fe-3.7(Nb + Ta)
Alloy 690	NO6690	30Cr-60Ni-9.5Fe-1(Nb + Ta)
Alloy 800	NO8800	21Cr-32.5Ni-46Fe-0.04C
Alloy 825	NO8825	21.5Cr-42Ni-3Mo-30Fe-2.2Cu-0.9Ti
Alloy 59	NO6059	23Cr-59Ni-16Mo-1Fe
Alloy 45TM	---	27Cr-47Ni-2.7Si-0.08N-Balance Fe
C276	N10276	16Cr-55Ni-16Mo-6Fe-4W
G3	NO6985	22.5Cr-43Ni-7Mo-20Fe-2Cu-Co
Alloy 903	N19903	38Ni-15Co-3Nb-1.4Ti-0.7Al-0.01C
Cobalt Alloy		
S816	---	20Cr-20Ni-47Co-4Mo-4W-4(Nb + Ta)
Aluminum Alloys		
Aluminum	A91025	A-1050, 99.5Al
Al alloy	A95052	A-5052, 97Al-2.5Mg-0.2Cr
Titanium Alloys		
Ti grade 1	R50250	Ti(α)
Ti grade	R56400	Ti-6Al-4V

YEARLY PLAN FOR THE IEA RESEARCH COLLABORATION PROGRAM

The IEA research collaboration program on deep geothermal developments is planned to start in March 1997 (Uchida and Kimbara, 1996). The research program, which has been proposed by Japan and will be undertaken by NEDO, will be divided into three subtasks. The subtask C is relating to material evaluation research work. The aim is to develop guidelines for materials selection for deep-seated geothermal resources.

A four year program of activities is proposed in the subtask C, see Figure 3. The first activity is to gather information on past, present and planned experiences, tests and research on materials in deep and aggressive geothermal systems, both published and unpublished. The second is to establish a group for exchanging experience on materials and chemistries. After that the obtained information will be summarized in a data book.

The third planned activity is to perform corrosion tests of materials in field trials and laboratory tests as are required to help in the materials selection process. The corrosion tests may include for example simulations of two-phase acidic flow or pressure vessel testing of materials in acidic fluids. Once the corrosion chemistry is defined it may also be possible to use existing data from other industries, for example flue gas desulfurisation plant used on energy boilers (Lichti and McIlhone, 1995). Data from tests in natural volcanic features will be used as a starting point for developing the materials guidelines (Saito et al., 1994, Kurata et al., 1995, Lichti et al., 1996).

All the information will be summarized in a report, which will provide a summary of existing data on fluid chemistry and performance of materials in deep geothermal developments and related environments. It will present guidelines for economic selection of materials for energy development processes and plant for corrosive deep geothermal environments.

Participation in the subtask C is encouraged for all geothermal developers concerned with acid well fluids. Currently participation has been agreed by Japan and New Zealand who are working together on two projects.

Figure 3. Yearly Plan of the Subtask C in the IEA Deep Geothermal Resources Task.

	1st (1997)	2nd (1998)	3rd (1999)	4th (2000)
1. Geochemistry	Data Base (Chemistry of fluids in geothermal environments)			
2. Materials and Their Failure				
3. Corrosion Model for high-temperature for two-phase flow	Corrosion Models			
4. Materials Slection				
5. Summary Report	Guidelines for Materials Selection			Int'l Journal
6. Other Int'l Meeting	NEDO Sympo (Japan)	GRC (USA) Workshop (NZ)	() ()	WGC2000 (Japan)

CONCLUSIONS

Discharge water and steam chemistries of deep-seated geothermal production wells are expected to contain significant concentrations of aggressive species CO₂, H₂S and HCl for example and may be of high salinity (high Cl) and low pH (high SO₄). These corrosion chemistries are demonstrated for example by the chemistries seen in some deeper wells in Japan and in shallow wells in the Philippines. The corrosion properties of these fluids have not been fully defined and there is a need to collect and evaluate materials results and experience relevant to the selection of materials for deep-seated geothermal developments.

The IEA Deep Geothermal Resources Task Subtask C Materials Evaluation Program was proposed to encourage information exchange and collaborative research activities. A four year program of activities has been outlined to progress this area of research. Further participation is welcomed.

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