RUSSIAN GEOTHERMAL SOURCES AND PROBLEMS OF METAL EROSION-CORROSION OF GEOTHERMAL POWER PLANTS .

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ABSTRACT

Russia has a large reserves of geothermal heat which can be used for electricity generation at geothermal power **plants.** Geothermal sources **of** Russian geothermal sites **are** highly mineralized (< 4.0 g/kg) with neutral pH = 6.0 - 9.0. Corrosion tests show that Russian metals are resistant enough when used geothermal equipment. Methods **of** inhibition of corrosion in geothermal fluids have been developed in Scientific and Training Centre **of** Moscow Power Institute.

At present 2.5 MW power-generating units have been manufactured, and five 23 MW units for San-Jacinto Geothermal Power Plant (Nicaragua) are under production. In 1995 - 1996 commissioning **of** 12 (4 x 3) MW Verkhne-Mutnovskaya Geothermal Power Plant (Kamchatka) is planned.

1. Geothermal Sources in Russia

Resource base of modern geothermal power plants are sites of steam/water thermal **sources** with coolant temperature above 160 °C [1]. Kamchatka and Kurile Islands are the most prospective in Russia in this respect.

Kuriles and Kamchatka are the young volcanic area and are distinguished for the maximum proximity of geothermal system to the surface **of** the Earth, what determines ecological advisability **of** their use.

According to estimation made by VSEGINGEO, reserves **of** steam/water thermal sources of Kamchatka and Kurile Islands are capable to drive geothermal power plants with total capacity up to 1,500 MW.

At present the following sites have been explored: Pauzhetskoye, Mutnovskoye, Bol'shebannoye, Okeanskoye (Fig. 1). The exploration **of** Nizhne-Koshelevskoye and Verkhne-Koshelevskoye sites, as well as on Kunashir and Paramushir (Kurile Islands) has been underway. Table 1 presents some geological and technical parameters of Kurile and Kamchatka sites.

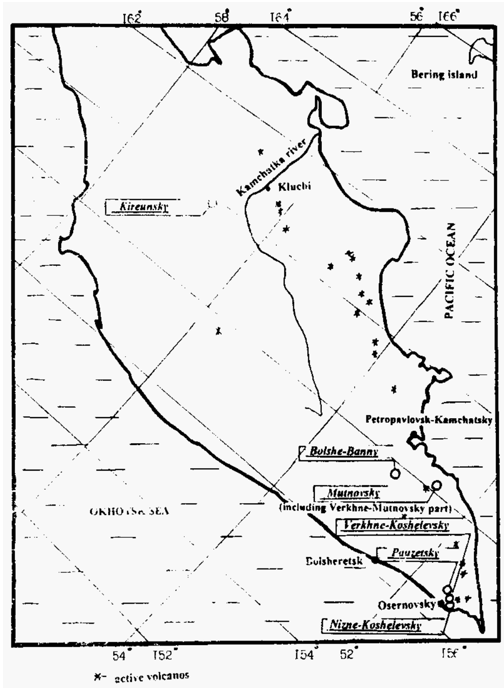

Figure 1. *Sites of steam/water thermal sources of Kamchatka.*

2. Quality of Coolant of Russian Geothermal Sites Suited for Geothermal Power Plants

<u>**Pauzhetskoye Site**</u> has steam/water thermal sources with temperature up to 210 °C. At present **9** production, 11 injection, and 13 observation wells are in operation. Maximum yield of the production well doesn't exceed 20

Table 1. *Some geological and technical parameters of Kurile and Kamchatka sites.*

No	Site (stage)	Coolant type	Site area, km^2	Average depth of wells, m	Average yield of wells, kg/s (steam)	Average steam content, %
1	Pauzhetskoye	SWM*	10	1,000	4	15
2	Mutnovskoye	Steam, SWM	22	1,300	6.6	45
3	Bolshebannoye	SWM	6	800	4	15
4	Nizhne-Koshelevskoye	Steam, SWM	11	1,500	6	40
5	Verkne-Koshelevskoye	Steam, SWM	11	1,500	6	40
6	Kireunskoye	SWM		800	4	10
7	Okeanskoye	Steam, SWM	12	700	4	35
8	Ebeko	Steam, SWM	12	700	4	30

*SWM - steam/water mixture

kg/s at enthalpy of 732 kJ/kg. Total flowrate in discharge zone is estimated as 300 kg/s. Pauzlietskaya Geothermal Power Plants with installed capacity of 11 MW is under operation at this site [2].

The coolant has sodium-chloride composition at pH = 6.8 - 8.0. Total mineralization reaches 3.0 g/kg; up to 50% being attributed to chlorides. Ca^{2+}, K^{+}, Mg^{2+}-ions, SO_4, and SiO_2 are present in liquid phase (Table 2).

Table 2. *Chemical composition of steam/water thermal sources of Pauzhetskoye Site, ppm.*

Composition of liquid phase	Content
Na^{+}	667
Ca^{2+}	143
Mg^{2+}	4.6
K^{+}	31
Cl^{-}	1,300 - 1,700
SO_4	70 - 80
Si02	200 - 300
Mineralization	2,416 - 2,926
Composition of gas phase, gas/steam, % vol	0.023
CO_2	83.8
H_2S	4.4
H_2	3.0

Gas composition of tlie coolant mainly consists of carbon dioxide and some hydrogen sulfide and hydrogen.

<u>Mutnovskoye Site</u> is located 70 km south-west from Petropavlovsk-Kamchatsky. About 60 wells have been drilled at this site, and one third of them are production wells. Reserves of geothermal coolant are capable to drive geothermal power plants with capacity of more than 250 MW.

Verkhne-Mutnovskaya Geothermal Power Plant with 3x4 MW capacity is proposed to be constructed by 1996, and construction of Mutnovskaya Geothermal Power Plant (tlie first stage 4x23 MW) is planned.

Geothermal coolant of the Mutnovskoye Site is dry and wet steam with temperature up to 245 °C and enthalpy up to 660 kcal/kg. Chemical composition of Mutnovskoye steam/water thermal sources is characterized as chloride, chloride-sulfate, and sulfate-chloride medium with the main sodium and calcium cations [3] (Table 3).

Table 3. *Chemical composition of Dachnoe Area of Mutnovskoye Site, ppm.*

Compounds	Wells yielding steam/water mixture	Wells yielding steam
NH_4	< 10.0	1.5 - 36.0
Na^{+}	30.0 - 310.0	< 16.0
K^{+}	4.0 - 28.0	< 48
Ca^{2+}	< 4.8	< 18.0
Mg^{2+}	< 6.6	< 2.4
Fe^{2+}	< 0.9	< 1.75
Cl^{-}	4.0 - 351.0	< 21.8
SO_4^{2-}	8.0 - 172.0	< 25.0
HCO^{3-}	16.0 - 98.0	< 100.0
SiO_2	8.0 - 712.0	< 104.0
HSO_2	0.6 - 69.0	< 4.2
CO_2	< 308.0	< 371.0
Miierali-zation	186.0 - 1,713.0	16.6 - 270.9
pH	5.2 - 9.4	3.45 - 7.0

Salt composition of the steam/water coolant of the Mutnovskoye Site is expressed by the following equation:

$$M_{0.6} = \frac{Cl_{62}\ SO^{4}_{22}\ HCO^{3}_{11}\ CO^{3}_{3}\ NH^{4}_{2}}{Na_{89}\ K_{8}}$$

and of the steam coolant:

$$M_{0.5} = \frac{HCO^{3}_{53}\ Cl_{26}\ SO^{4}_{21}}{NH^{4}_{63}\ Na_{20}\ Ca_{12}\ Mg_{3}\ K_{2}}$$

Gas composition of the coolant mainly consists of carbonic acid (up to 70%vol CO_2). Besides, there are hydrogen sulfide, nitrogen, oxygen, methane, hydrogen. Volume content of hydrogen sulfide is 10% in average. Table 4 presents data on content of non-condensing gases in the coolant of the Mutnovskoye Site.

Table 4. *Content of non-condensing gases in geothermal coolant of Dachnoe Area of Mutnovskoye Site.*

Non-condensing gases	Gas content, % vol	
	Wells yielding steam/water mixture	Wells yielding steam
CO_2	< 61.0	56.0 - 71.0
H_2S	5.7 - 14.3	7.2 - 14.5
N_2	9.6 - 13.7	8.2 - 13.7
CH_4	< 2.0	< 2.02
NH_3	< 0.9	< 1.5
O_2	< 19.7	< 2.4

<u>Okeanskoye Site</u> is located on the slope of Baransky Volcano in the basin of Sernaya River at a distance of 17 km from Kuril'sk (Iturup Island). More than 10 wells have been drilled at the Okeanskoye Site. According to data of PGO "Sakhalingeologiya", reserves of steam/water thermal sources of the Okeanskoye Site are capable to drive geothermal power plants with capacity of about 60 MW.

Constructioii of the first stage of Okeanskaya Geothermal Power Plant with installed capacity of 3x4 MW is planned.

Phase state of coolant froni different wells varies considerably (moisture content varies from 0 to 70%), yield of wells is 1.0 - 12.0 kg/s.

Table.5 presents chemical composition of liquid phase of steam/water mixture of typical wells of the Okeanskoye Site.

Table 5. *Chemical composition of liquid phase of steam/water mixture of typical wells of the Okeanskoye Site, pptn.*

Parameter	Well no.		
	51	52	57
Na^+	1.219	21	737
K^+	265	1	133
$Ca_2{}^+$	23	1	4.5
$Mg_2{}^+$	48		2
Cl^-	2,284	4	1,333
$SO_4{}^{2-}$	26	75	20
$HCO_3{}^-$	21	24	18
Si02	126	10	129
H_3BO_4	126	33	86
H_2S	11	1.5	14
Mineralization	4,138	156	2.506

Gas composition of the geothermal coolant of some wells of the Okeanskoye Site is given in Table 6.

Table 6. *Non-condensing gases in geothermal coolant of typical wells of the Okeanskoye Site, % vol.*

Parameter	Well no.		
	51	52	57
CO_2	40.3	59.6	54.5
N_2	41.6	8.9	11.9
CH_4	6.8	19.2	18.1
H_2	6.4	4.4	10.3
H_2S	3.1	7.2	4.2
SWM flowrate, kg/s	7.0	3.2	2.9
pH	6.8	7.4	6.8
Temperature, °C	167	161	162
Moisture content, %	46	5	16

Kayasulinskoye Site is located in Stavropol Region. Here experimental two-circuit 3MW geotherinal power plant is constructed [4]. Depth of wells at tlie Kayasulinskoye Site reaches 4,200 m. Reservoir temperature is 170 "C, and mineralization is 100 g/kg.

Ion coniposition of dissolved impurities is given in Table 7.

Table 7. *Ion composition of impurities in coolant of the Kayasulinskoye Site, g/kg*

Ions	Content
Na^+	26.65
Ca^{2+}	8.62
Cl^-	62.39
Others	1.48
pH	5.7

3. Corrosion Tests

Corrosivity is the most important parameter of geothermal coolant wliicli in certain extent determines reliability and durability of equipment of geothermal power plants. Studies of corrosioii resistivity of Russian materials in geotlieriiial fluids have been carried out in Russia over several years.

Field tests of metals were carried out at the Mutnovskoye Site. The test results are presented in Table 8 [5].

Table 8. *Results of field corrosion tests of metals in steam/water mixture, steam, arid separated moisture at the Mutnovskoye Site (after 1,160 h), μm/year.*

Metal		Geothermal fluid		
Type	Main alloy components	SWM (135°C)	Steam (125°C)	Separated moisture (85 - 95°C)
Steel 3		5.4	23.4	10.1
10KhSND	0,66Cr;0,6Ni	4.4	20.4	9.5
06Kh12N3D	13,2Cr;3,2Ni	1.8	0.66	
08Kh18N10T	18Cr;9,6Ni	0.35	0.2	0.9

Rate of corrosion for studied steels turned out not to be high; it didn't exceed 25 μm/year. It is explained by a relatively low mineralization. The rate of corrosioii in separated moisture is slightly lower than in steaiii. An analysis of kinetics of metal failure testifies that control stage in form of oxygen depolarization exists.

Salt depositions were not found on the studied pieces. Chrome and alloyed steels had a solid oxide film. Loose corrosion products, together with tlie oxide filni, were found on carbon steel.

Corrosion and electrochemical paraiiieters of 15Kh11MF steel were studied jointly by STC Geo MEI aiid FMI on the model of geothermal fluid of the Mutnovskoye Site [6]. At 20 °C and without hydrogen sulfide steel corrodes with mixed oxygen-hydrogen polarization, where oxygen polarization prevails. If anode polarizatioii curve on some sections cari be approximated by Tafel curves (Fig. 2, curve 1), then cathode curve has a pattern typical for limiting diffusion current (Fig. 3, curve 1'). Steel corrosion potential is set in pseudopassivity region.

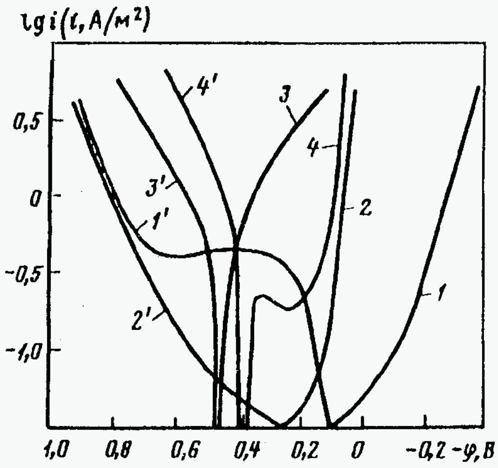

Figure 2. *Potentiodynamic polarization curves of 15Kh11MF Steel in geothertnal water at 20 °C (curves 1, 1', 3, and 33 and 90 °C (curves 2, 2', 4, and 43, and with hydrogen sulfide (curves 3, 3', 4, and 43: 1-4 - anode curves; 1'-4' - cathode curves.*

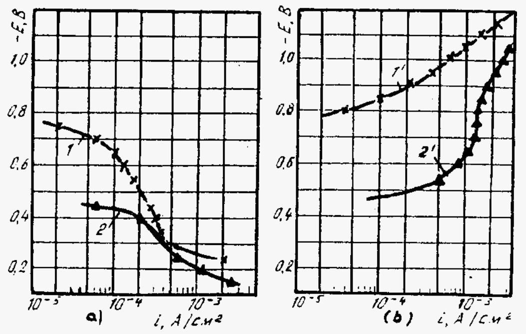

Figure 3. ***Anode (a) and cathode (b) polarization curves of 12KhIMF steel in geothermal fluid model of the Okeanskoye Site at SO °C : I - without stirring;2 - 4,600rpm.***

Increase in temperature **up** to 90 °C changes pattern of the polarizatioii curve: the anode curve shifts to negative potentials, **aiid** section corresponding to the limiting diffusion current **on** oxygen disappears from the cathode curve. **In** this casc the anode process is the determining factor.

of rotating disc electrode. At frequency of rotation of 4,600 rpm ***Re*** was 3x10E3.

Figure 3 shows typical anode and cathode polarization curves of 12Kh1MF steel without stirring and during rotation of tlie electrode at temperature of 50 "C. Hydrodynamic (erosion) action provides intensification of corrosion due to transport of chemicals to metal surface and destruction of film of corrosion products, i.e. influencing **on** factors on coiicentration polarization. Fluid motion results in shift of polarization curves to higher current densities.

The results of corrosion tests provided selection of tlie follwing Russian metals for productioii of geotlieriiial equipment:

- steel 25 (steel 20) for casing of separators and turbine;
- steel 20 for steaiii piping;
- 34KhN3M for turbine rotor;
- 12Kh13 for turbine blades;
- 30Kh13 for valves flowpath.

Table 9. ***Results of the study of stell corrosion resistance at the Okeanskoye Site.***

Steel		Rate of total corrosion, μm/yr			Maximum pitting depth, μm		
Type	Main alloy components	Well no. 51	52	57	Well no. 51	52	57
Carbon and low-alloyed steels:							
Steel 3		18	14.3	8.3	0	0	0
10KhNDP	0,6Cr;0,37Ni	19	18.3	8.5	0	33	0
Chrome steels:							
08Kh14MF	14Cr;0,3Ni;0,3Mo	1.5	0.9	0.6	48	30	24
15Kh18M2B	18,0Cr;2,0Mo	0.94	0.8	0.6	21	21	3
Chrome-Nickel hvo-phase austenite steels:							
12Kh18N1OT	18Cr;10Ni;1,0Ti	1.42	0.68	0.44	30	9	3
08Kh17N13M3T	17Cr;13Ni;3Mo;1Ti	1.2	0.44	0.30	48	0	3
04Kh25N6M3B	25Cr;6Ni;3Mo	0.23	0.23	0.22	0	0	0

Saturation of solution with hydrogen sulfide leads to sharp increase in rate of anode dissolution of steel and cathode release of hydrogen. It results in one order of corrosion current increase. Reduction of pH in this case froni 6.1 to 4.0 testifies that the hydrogen polarization prevails.
Corrosion tests of Russian steels were carried out at tlie Okeanskoye Site by STC Geo **MEI** and TsNIITMASh. The pieces were subjected to steam taken from three different wells (no. 51, 52, and 57 - chemical composition is given **in** Tables 5 aiid 6). Steam flowrate in containers didn't exceed 3 m/s, what allows to disregard erosion factors and consider loss of weight of the pieces as result of corrosion. Table 9 gives test results (exposure time was 92 days).

The highest corrosion rates (up to 20 μm/year) correspond to low-alloyed metals. In this case carbon steel (Steel 3) has slightly less corrosion rate to compare with low-alloyed steel 10KhNDP. Besides, it isn't subjected to pitting.

A relatively high corrosion resistance - oiie order less than for carbon steel - was found for chrome steels. Tlie rate of corrosion of chrome-nickel austenite steels is even less. But chrome and high-alloyed steels have an elevated tendency to pitting.

Study of erosion-corrosion impact of the model of geothermal fluid was carried out in laboratory conditions at FMI together with STC Geo MEI. Erosion and electrochemical parameters of 12Kh1MF steel in solution simulating the fluid of the well no. 51 were studied with the use

4. Inhibiting of Steel Corrosion in Geothermal Fluids

Over many years MEI develops and improves methods **of** reduction of corrosion and prevention of depositions in equipment of conventional [7] **and** geotliernial power plants. Recent results of similar joint studies by MEI and FMI are given below.

Inhibiting properties of surface-active substance **SA-I** studied in the model geotliernial fluid of the Okeanskoye Site. Kinetics of stabilization of electromotive force of metal plate (Steel 20)-chlorosilver electrode system was recorded at teiiiperature 85 °C and different SA-I concentrations (50, 500, aiid 1,000 ppm). Experiments showed that 0.05% SA-I resulted in significant reduction of **potential** (by 0.1 v) (Fig. 4). Deviation from this concentration to any side increased tlie potential.

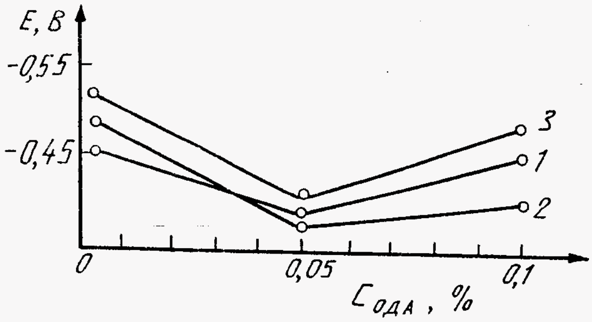

Figure 4. ***Concentration dependence E during exposure of Steel 20 in geothermal water model of &he Mutnovskoye Site (I - 1 h; 2 - 2 h, and 3 - 3 h).***

Change of the potential caii be explained by colloid-and-chemical behavior of the inhibitor. Amino **group** imparting **to it** diphyl properties promotes formation of mycels. Gradient of inhibitor content increases as the metal surface is approached. It provides good reasons for the formation **of** mycels and promotes noticeable drop of potential. Increase in SA-I content up **to** 0.1% results in the potential rise.

Voltamper curves (Fig. 5) obtained on clean polished surface of Steel 20 pieces in presence of 0.05% SA-I show that the presence of inhibitor results in two orders decrease in the corrosioii current.

The inhibitor **SA-**I considerably reduces absorption of steel with hydrogen due to formation of adsorption film. **At** 100 ppm hydrogen permeability is particularly sharply reduced, and current density decreases by oiie order (Fig. 6).

The inhibitor **SA-**I proved to be an excellent layup chemical. It precipitates from solution aiid formes on metal surface stable and solid protective film. After solution d;~-charge the protective properties are preserved for a long time, protecting metal from atmospheric corrosioii. Besides. **SA-I** has "washiig" properties. It allows to use it for washing of equipment from deposits.

At present testing of **SA-I** on operating equipment of Pauzlietskaya Geothermal Power Plant are under preparation.

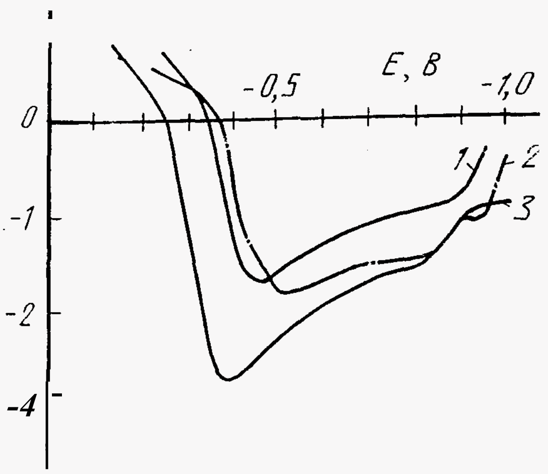

Figure 5. ***Voltamper curves of Steel 20 pieces in geothermal water model of the Mutnovskoye Site:***
1 - clean surface of pieces
2 - polished surface of pieces
3 - polished surface of pieces with 0.05% SA-I.

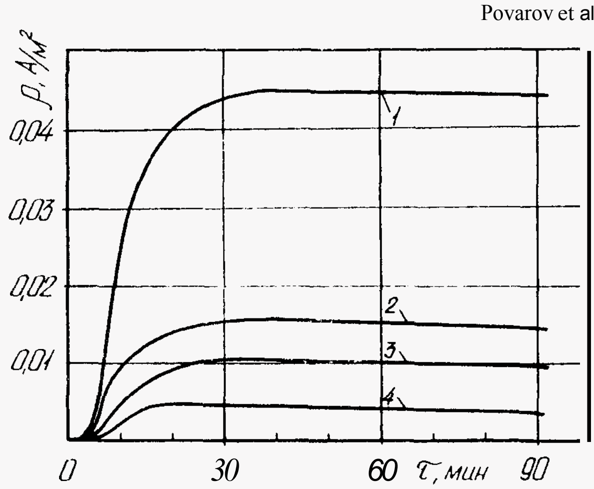

Figure 6. ***Hydrogen permeability of armko-iron in NaCl solution saturated with H_2S (30 °C): 1 - without protection; 2 - inhibitor content 5 ppm; 3 - inhibitor content 20 ppm; 4 - inhibitor content 100 pptn.***

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