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Corrosion and Material Selection for Geothermal Systems

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ABSTRACT

As geothermal energy is being developed and taking more importance, certain problems have occurred regarding the corrosion and the usage of the materials that are influence the effectiveness and the quality of the service. The knowledge of the characteristics of the geothermal fluid partly leading to the breakdown of the equipment used for processes due to corrosion, is very important in the equipment selection. Dissolved CO_2, H_2S, NH_3 and chloride ions, may lead to the metallic materials being corroded and becoming unusable. The chemical composition, temperature, and velocity of fluid vary depending on the geothermal resource, the design of the power system, and the point of the production cycle. Both the operating experiences gained during usage and laboratory studies performed with real geothermal fluids form the basis for the selection of materials for this area. In this paper, the reasons for the corrosion types that are seen in geothermal systems are discussed, and the evaluation of the behavior of the materials according to the environmental conditions where the metallic and nonmetallic materials are found. Precautions have to be taken in order to utilize materials like steel, stainless steel in geothermal industry. Titanium, Inconel, and Hastolloy C-276 Ni-Cr-Mo alloys could be preferable for high temperature geothermal use. Concrete-polymer compounds, cement and fiber reinforced plastics and other non-metals are more useful because of their high corrosion resistance and reasonable cost especially for the geothermal heating using low-enthalpy fields.

1. INTRODUCTION

Geothermal fluids contain dissolved CO_2, H_2S, NH_3 and chloride ions that can cause corrosion of metallic materials, therefore safe utilization of geothermal systems depends importantly on materials selection.

Precautions during the design step, and conscious material selection, have an important role to minimize the effects of corrosion. Optimum cost and safety are factors influencing material selection. Construction costs, operation wealth, operation costs, production lost costs, and reparation costs affect material selection directly. Operational experience in geothermal fields and laboratory research using real geothermal fluids form the basis for material selection. In this article, corrosion types and causes encountered in geothermal systems, and the environmental conditions of metallic and nonmetallic materials in geothermal systems have been considered.

2. GEOTHERMAL SOURCES AND POWER CYCLES

The thermodynamic power cycle is a process that is used to convert geothermal energy into electrical energy. The methods used to rotate a turbine by obtaining wet steam or dry steam depend on the properties of geothermal fluid. Geothermal sources are classified into four types; steam dominated, liquid dominated, hot dry rock and geopressured sources. There are power cycles for these sources. Power cycles are classified according to whether the fluid is steam dominated, or liquid dominated or whether the wells are artesian or not. Power cycles consist of three steps; obtaining geothermal fluid from a well, rotating the turbine by obtaining wet steam or steam, and condensing gases.

3. CORROSION TYPES ENCOUNTERED IN GEOTHERMAL SYSTEMS

UNIFORM CORROSION:

Uniform corrosion occurs equally throughout the metal surface. In geothermal systems it is generally due to chloride, ammonium or hydrogen ions.

PITING CORROSION:

It is the corrosion type in which pits occur through the metal surface. Pits frequently deepen due to the breakage of a passive film. The beginning of pit formation and the rate of deepening cannot be predicted.

CRACK CORROSION:

It is similar to pit corrosion when formation type is concerned. Apart from other corrosion types it depends on geometry. It is observed under the accumulation layers of metallic materials that occur during equipment production or operation conditions. Beginning and depth cannot be predicted.

STRESS CORROSION CRACKING (SCC):

It is a dangerous type of corrosion occurring due to the chloride ions and stress in the metallic material. Presence of oxygen and the increase in temperature increase the corrosion rate.

SULPHUR STRESS CORROSION CRACKING (SSC):

It is the corrosion type occurring due to the presence of high strength steel in the moist environment containing Hydrogen Sulphide (H_2S). It is different from stress corrosion cracking since corrosion rate decreases with presence of oxygen and temperature increase in sulphur stress corrosion cracking. Moreover low pH values increase the corrosion rate.

HYDROGEN BUBBLING:

It occurs due to the presence of low strength steels in aqueous solutions containing hydrogen sulphide. Fractures occur because of the insufficient movement of hydrogen caught in vacancies. It is not necessary to apply stress to the material for this type of corrosion.

INTERGRANULAR CORROSION:

It is the regional corrosion that occurs around the grain boundaries or in the neighbour grains of metallic materials; however it does not affect the grains. Alloy fractures or loses strength. Wrong heat treatments cause this type of corrosion.

GALVANIC CORROSION:

Galvanic corrosion occurs by the electrical conduction of two different metals. By considering the galvanic series endurance list can be done in material selection. However in the chemical systems and by change of temperature endurance list may change.

FATIGUE CORROSION:

Fatigue corrosion occurs due to the fluctuating stress in a corrosive environment. Fatigue corrosion limit is the largest stress under given conditions. The combined affect of fluctuation, stress and corrosion is much larger than the other simple effects.

EROSION CORROSION:

It is the abrasion of the metallic material by the striking of high velocity fluids to the hanging solid materials or particles. The metal that is exposed to this kind of corrosion does not form corrosion product on its surface. Along the flow direction, pits can be seen by the naked eye, and circles form in the shape of waves. It is frequently seen at the turbine blades and in the fields having the flow of two phases.

DECOMPOSITION OF ALLOY STRUCTURE:

It is the dissolution of one component of the alloy.

CAVITATION:

Cavitation is a fast and regional decomposition around the metal surface caused by the exploding steam bubbles.

4. VARIABLES AFFECTING THE CORROSION RATE

There are various variables affecting the corrosion rate of the geothermal fluid. These are; pH, dissolved oxygen, carbon dioxide, hydrogen sulphide, ammonia, sulphate, chloride and suspended solid material and its deposit. The effects of these variables are summarized here.

pH EFFECT:

Corrosion rate of carbon steel increases as pH decreases. This situation is especially seen when pH environment decreases below 7. Passivity of many alloys depends on pH. In local regions, corrosion increases with passivity breakdown. By pit corrosion, crack corrosion and stressed corrosion cracking may occur.

EFFECT OF CHLORIDE IONS:

Presence of chloride ions causes the breakage of the passive layer that prevents many metals from corrosion. By the breakage of this layer, pit corrosion and cracking with stressed corrosion occurs.

EFFECT OF HYDROGEN SULPHIDE:

Hydrogen sulphide basically affects copper and copper-nickel alloys. Although usage of copper and copper-nickel alloys is advantageous in sea water environments, they are not preferred in geothermal fields because of the corrosion effect. In iron-based materials they are harmful above concentrations of 50 ppm. High strength steels are generally exposed to stress corrosion cracking by the effect of hydrogen sulphide. Hydrogen sulphide also creates hydrogen bubbling in steels. If geothermal process fluid contains dissolved oxygen, hydrogen sulphide is oxidized with this oxygen and by decreasing pH of the geothermal fluid, it increases the corrosive features of the environment.

EFFECT OF DISSOLVED CARBONDIOXIDE:

Increase in the dissolved carbon dioxide amount in geothermal fluid causes pH to decrease by providing acidic influence in the environment. Low carbon steels cause uniform corrosion in materials. pH of the geothermal fluid and flow of the process mostly depends on the carbon dioxide amount. Presence of carbonate and bicarbonate or their formation causes a slight decrease in corrosion rate.

EFFECT OF AMMONIA:

Ammonia causes cracking of copper alloys by stress corrosion. Causes uniform corrosion in soft carbon steels.

EFFECT OF SULPHATE IONS:

There is no significant effect of sulphate ions on geothermal fluids. In the fluids containing low amount of chloride ions, sulphate acts as the main attacker ion but it can not be very effective.

EFFECT OF DISSOLVED OXYGEN:

When low amount of oxygen enters to the geothermal systems operating at high temperatures, normal resistant metals undergoes stress corrosion cracking. Oxygen amount of the system must not be below 20ppb. Low carbon steels are sensitive to the corrosion above this limit.

EFFECT OF SUSPENDED SOLİD MATERİAL AND DEPOSITS:

The existence of suspended solid materials in the geothermal fluid or precipitation of ions by chemical reasons causes deposit formation on the materials. Solid materials and deposits create erosion corrosion.

5. THE PERFORMANCE OF THE METALS IN GEOTHERMAL SYSTEMS

The operation experiences and the field tests in different geothermal system applications provide an opportunity to evaluate the material performance. These evaluations are given for liquid, condensed and vapour contacted geothermal systems.

5.1. Metallic Materials

Soft and low alloyed metals

Because of their low expense and convenience, low carbon steels seem to be a sensible material; on the other hand, safe usage of this material depends on the applications in the system. Soft steels can be used, by taking the necessary precautions in thick walled systems. The usage of these steels is limited in thin walled systems because of the risk of crack and pit corrosion. Uniform and local types are the frequently encountered corrosion types as a result of the usage of soft steels. As a result of the various field tests, it is observed that in the circumstances where pH value is greater than 6 and the Cl ion concentration is lower than 2%, the uniform corrosion rate varies between 1 and 10 mpy. For geothermal fluids, local corrosion is more effective than the uniform corrosion. Cl ion triggers the local corrosion. Presence of hydrogen sulphide in the environment increases the effect of local corrosion. Low amount of oxygen in the environment also accelerates the uniform corrosion formation hence triggers the occurrence of pit and crack corrosion. High flow rates and solid particles accumulated in the fluids result in erosion corrosion. The optimum flow rate for carbon steel materials is 5-7 fps (1). Because of the chemical properties of the geothermal fluid, some ions precipitate and accumulate on the surface of steel. These accumulations have pores and tendency to cracking. Corrosion may occur in these small areas. In the case of release of those accumulations from the steel surface and with the presence of Cl ion, local corrosion occurs. Protective plating can be used for outside surfaces to prevent the uniform and local corrosion. Sulphur stressed breaking can be seen in steel materials which are subjected to hydrogen sulphide under stressed condition water environment (1) (2). It increases with the increase in temperature, decrease in stress, decrease in strength, and decrease in the concentration of sulphur and increase in pH. Steel materials that include more than 1 % of nickel are more sensitive to this condition. Besides, hydrogen bubbling may occur in the low strength steels which are subjected to water solutions having hydrogen sulphide. Room for bubbling is necessary. Consequently, steels not having much room for this procedure are more resistant to bubbling (1).

Stainless Steels

Stainless steel material decreases the probability of uniform corrosion formation in geothermal fluid environment. However, more serious corrosion problems may occur. These are; pit corrosion, cracking corrosion, breaking with stressed corrosion, breaking with sulphur stressed corrosion, corrosion between the particles and wearing corrosion. Cracking corrosion can be a serious problem for stainless steel when used with sophisticated equipment in geothermal fields. An increase in the Cl ion concentration in the environment results in an increase in the effect of local corrosion. Rising temperature increases the pit potential. The resistance of stainless steel against pit and cracking corrosion depends on its chrome and Mo content. These two elements increase the resistance of stainless steel in an environment without oxygen. Austenitic stainless steels are vulnerable to breaking with stressed corrosion in the presence of Cl ion at high temperatures. Ferric stainless steels are generally stronger. Breaking with stressed corrosion depends on Cl ions, oxygen concentration, pH value, temperature, and tension and alloy components. Alloys with nickel can be affected by stressed corrosion. Addition of Mo and silica increases the resistance to stressed corrosion (1). Corrosion between the particles can be seen in austenite and ferric stainless steels. Especially during the welding operation this may be observed. Ferric stainless steels can be influenced by sulphur stressed breaking but austenite stainless steels can not. Low strength steels are more vulnerable to sulphur stressed breaking. AISI 400 series stainless steels contain 12-18 % chrome. This has a great importance for turbine blades, pump and valve materials. 13 % chrome is suitable for turbine blades. AISI 430 (Ferrite) and AISI 431 (Martensitic) stainless steels types are often used for valve and pump components in geothermal systems. In order to prevent the pit corrosion and breaking problems in wellhead valves, geothermal fluids containing high amounts of Cl ions, sulphur and oxygen in solution, it is more suitable to use AISI 430 (Ferrite) (3). Thermally treated martensite stainless steels are preferred for pump inside components and shafts. AISI 300 series stainless steels show well performance in geothermal condensates at low temperatures and geothermal fluids not containing oxygen (4).

Titanium and Titanium Alloys:

Titanium and titanium alloys are more successful when they are used with air-cooled or oil-cooled heat exchangers. Corrosion rates of titanium materials which are experimented with geothermal fluids are generally lower than 0.3 mpy. It is proved with the experiments that increases in temperature and Cl ion concentration do not accelerate the corrosion rate. It is also observed that flow rates about 30 fps do not affect the general corrosion. Besides, titanium is resistant to cavitation and impact damages. Pit and cracking corrosions are observed at high temperatures and for Cl ion concentrations above 10 % (1) (2). Titanium alloys are much more resistant to local corrosion than pure titanium. Ti-code-7 (Ti-0.15 Pd), Ti code-12 (Ti-0.3 Mo-0.8 Ni), and Ti-code-29 (Ti-6 Al-4 V-0.1 Ru) show well resistance. Titanium is more cathodic than other metals. If the titanium area is greater than the paired metal, the paired metal undergoes galvanic corrosion seriously. Titanium can form hydrogen when it is paired with active metal because of the cathodes in a galvanic pair. Titanium may absorb the hydrogen and that results in hydrogen embrittlement. It is assumed that titanium alloys are vulnerable to breaking with stressed corrosion in Cl ion concentrations above 3%.

When they are compared on the basis of cost and performance, titanium alloys can be used properly as other stainless steel alloys. Titanium alloys can be used when the Cl ion concentration of the geothermal fluid is greater than 5000 ppm and the temperature above 100˚C (6). Furthermore, they are preferred as material when there is oxygen entrance to the system, because geothermal fluid containing oxygen and hot Cl ion can cause breaking with locally corrosion for stainless steel and nickel based alloys. In these circumstances, the critical places for the use of titanium alloys as the material can be; wellhead valves, pressure gauges, pipes and blow-out preventers. If the amount of dissolved solid material of hot geothermal fluid containing Cl is above 100,000 ppm, pH is lower than 4 and the wellbore temperature is above 230˚C, titanium code 29 pipes are preferred for the transportation of the geothermal fluid. The service life of this material is above 15 years and it does not have renewable costs compared to low alloy steel and in addition they do not form corrosion and accumulation products containing radioactive and heavy metals. Furthermore, they reduce the risk of well plugging and well damaging and prevent the plugging of well pipes with iron-enriched silicate accumulations. Titanium code 29 is being used as well lowering pipe in USA Salton Sea. (5)

Nickel Alloys:

Corrosion often calls for the frequent usage of nickel alloys. For the high temperature geothermal fluids, it is suitable to use Ni-Cr-Mo alloys as a material (6). Especially, Inconel-625 and Hastelloy C-256 are very strong for the corrosion (1), (2), (4). Instead of molybdenum, similar alloys, which have iron elements, can be used in some applications because of its mechanical properties and the reason that it is also much stronger than the stainless steel. Some nickel alloys lack resistance to the stress sulphur cracking or to the hydrogen embrittlement in the presence of hydrogen sulphide. Furthermore, Ni-Cu alloys are not suitable even in low hydrogen sulphide conditions

Copper Based Alloys:

It is limited to use copper alloy materials with geothermal fluids that have high amount of sulphur. It has been known to see cracks in the copper alloys which faces with the ammoniac and something like ammoniac. Some cases when the amount of ammoniac and ammonium are low, the cracks on the metal surfaces are limited (1), (2). The breakup risk in the copper-zinc alloys increases with the increasing of the amount of zinc.

Copper and copper alloys have been tested for the heating systems (3). It is established that copper fan bobbin and heat exchangers with copper tubes show a low performance for the corrosion in the presence of sulphur compound in the geothermal fluids. Similar to previous result, another research on the heat exchangers shows that copper-zinc (brass) and copper-tin (bronze) alloys are not suitable for the corrosion. It is found that red lead brass alloy (CA 836 and 838) and red lead bronze alloy (SAE 67) materials can be used for the inside of the pump (3).

Other Metal-like Materials:

The other materials and alloys are limited in this area. Cobalt alloys can be used in the application, which need resistance, of high durability for the abrasion strength and stress sulphur cracking (1), (2). It can be used in the part of zirconium and tantalum acidizing. It is observed that aluminum alloys have low performance in the direct contact of geothermal fluids (1), (2), (4). In these alloys, hollow and galvanic corrosion can be frequently seen.

5.2 Non-Metallic Materials

Generally, metals are used as material in the geothermal fields. On the other hand, the usage of non-metallic materials increases day by day. The usage of this non-metallic materials are needed in some special geothermal operations and drilling operations, such as the use of elastomers. Besides, there are some advantages of non-metallic materials: they are generally strong for the corrosion when they are encountered with metals and alloys. The initial investment cost is lower than metals and alloys because of the long period of operating and repair. However, they are not useful in heat transfer equipment. The specifications of some non-metal materials which are used in geothermal field and their properties are given below (1),(2),(4),(6),(7):

Concrete and Polymer Composition: The endurance of Polymer Concrete depends on all composition. Polymer Concrete materials, which are include silica, sand and portland cement, are enduring geothermal water and steam over 218 ^{o}C.

Cements: C-S cements and phosphate glass cements are investigated as potential cementing material. The cements, which are resistant for the corrosion, can be used as coating materials.

Elastomers: The investigation of elastomers has been continuing in the drilling operations. Nowadays, the usage of elastomeric materials as connection components comes on the agenda in pipelines. Fluorine-elastomer shows the best performance as a connection component in pipelines. Neoprene and natural rubber could not be successful in this area. Ethylene-Propylene-diene terpolymer is used as sealing in valve and o-ring in most systems.

The fibre reinforced materials: The usage of Chlorinated Polyvinyl Chloride (CPVC) and Fiberglass Reinforced Plastic (FRP) increases because of high resistance of corrosion and low cost. Especially, it is used safely in corrosive geothermal water transport lines. Fiberglass Reinforced Plastic (FRP) pipelines are supplied at low cost by means of smooth surface in central geothermal heating systems and water and hot water transport lines. Moreover, Fiberglass Reinforced pipelines decrease the usage of scaling inhibitor and supplies low cost by means of smooth surfaces because of low contact of CaCO3 to the pipeline surface in high CaCO3 settlement. The mechanical properties of Fiberglass Reinforced Plastic (FRP) pipes, its durability in high pressure (>200 bar) and its durability in high temperature (>130 ^{o}C) improved with the last studies. In addition, when they are used with mistakes, it creates some problems, such as brittleness and breakoff. Because of that, material producers should consider the project at which the material will be used, the design and the management conditions. The most important criterion about the life-time of Fiberglass Reinforced Plastic (FRP) pipeline is the assembly situation. In the case of wrong assembling, the breakoff and brittleness are inevitable.

6. CONCLUSIONS

In geothermal systems, probable corrosion models should be put forward by analyzing the system before the design and material selection procedure. The corrosion model should be developed under wellhead and wellbore conditions and should include corrosion chemistry and the effect of the fluid flow rate on erosion corrosion. Hence, suitable material selection and corrosion control for the design would be obtained. Although low alloy steels are mostly preferred as easy to obtain and low in expense, the necessary precautions should be taken in order to use them safely in geothermal systems. The probability of stainless steels to undergo uniform corrosion is low, when they are used with geothermal fluids. On the other hand, some other types of corrosion may be observed. Stainless steel material selection and usage should be made carefully. Titanium and titanium alloys are resistant to pit and cracking corrosions at Cl ion concentrations below 10%. Their usage in air or oil cooling heat exchangers is suitable. However, at high temperatures they undergo pit corrosion. Inconel-625 and Hastelloy C-276 are the most suitable Ni-Cr-Mo alloys for use in high temperature geothermal fluids. Cobalt alloys are used for applications which require resistance to abrasion resistance and sulphur stressed compression, and high strength. Zirconium and tantal alloys are used with channels subjected to hot hydrochloric acid treatment. The performance of aluminum alloys is pure because they form galvanic and pit corrosions. The usage of concrete-polymer mixtures which are classified as non-metallic material, and Fiberglass Reinforced Plastic (FRP) pipes and materials, has been rapidly increasing. The applications of Fiberglass Reinforced Plastic (FRP) materials in central geothermal heat systems by investors and managers are rapidly increasing due to their high corrosion resistance, easy of installation and short time for assembly, longer service life and low operating costs.

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