4. CHEMISTRY OF THERMAL FLUIDS

Geothermal fluids contain a wide variety and concentration of dissolved constituents. The simplest chemical parameters often quoted to characterize geothermal fluids are:

1. Total dissolved solids (TDS) in parts per million (ppm) or milligrams per liter (mg/L). This gives a measure of the amount of chemical salts dissolved in (he waters.

2, pH- The pH of a fluid is a measure of the acidity or alkalinity of the fluid. Neutral fluids have pH = 7 at room temperature. Acid fluids have pH values <7 and alkaline fluids have pH values >7.

These two parameters can be measured in the field by use of a conductivity meter and a pH meter. The conductivity meter measures the TDS of a fluid by measuring its electrical conductivity. The more dissolved salts, the higher the electrical conductivity.

The amount and nature of dissolved chemical species in geothermal fluids are functions of temperature and of the local geology. Lower-temperature resources usually have a smaller amount of dissolved solids than do higher temperature resources, although there are exceptions to this rule. Prolonged water-rock interaction liberates ionic species and produces a saturated silica solution (tab.4.1).

TDS values range from a few hundred to more than 300,000 mg/l. Many of the high-temperature resources in the west contain 6,000 to 10,000 mg/L TDS; whereas, a portion of the lmpenal Valley, California resources are essentially saturated with salts at 300,000 mg/l. The pH of geothermal resources ranges from moderately alkaline (8.5) to moderately acid (5.5). The dissolved solids are usually composed mainly of sodium (Na), calcium (Ca), potassium (K), chlorine (Cl), silica (SiO_2), sulfate (SO_4), and bicarbonate (HCO_3). Minor constituents include a wide range of elements with mercury (Hg), fluorine (F), boron (B) and arsenic (As) being toxic in high enough concentrations and therefore, are of environmental concern.

Table 4.1 - Typical composition of geothermal waters

| Species | Wairakei[2] | Rotorua[3] | Waitoa[4] | for comparison | |
	wells ~ 1.5km	springs	springs	Seawater[5]	River water
Cl-	2156	560	57	19350	5.7
Na+	1200	485	220	10760	4.8
SiO_2	660	490	175	0.005-0.01	13
K+	200	58.5	43	399	2
HBO_2^-	115	21.6	1.2	0.004	-
HCO_3^-	32	167	3177	142	23
SO_4^{2-}	25	88	<1	2710	6.7
Ca^{2+}	17.5	1.2	37	411	15
Li+	13.2	4.7	0.6	0.18	-
F-	8.1	6.4	0.3	0.0013	-
NH_3	0.15	0.2	-	-	-

[1] figures given in ppm, where ppm = mg/kg; [2] "neutral chloride" waters; [3] "acid sulfate" waters; [4] "alkali carbonate" waters; [5] seawater has a pH range of 8.1-8.3 and river water has a pH range of 5-6.5

In general, each state has regulations governing the use and disposal of waters that contain toxic or otherwise harmful constituents, and local regulations should always be consulted in planning the use of any geothermal resource. Dissolved gases usually include carbon dioxide (CO_2), hydrogen sulfide (H_2S), ammonia (NH_4) and methane (CH_4). Hydrogen sulfide (H_2S) is a safety hazard because of its toxicity to animals, including humans. Effective means have been and are

still being developed to handle the scaling, corrosion, and environmental problems caused by dissolved constituents in geothermal fluids.

As geothermal fluids move through rocks, they react chemically with the rocks, which themselves are usually chemically complex. Certain minerals in the reservoir rocks may be selectively dissolved by the fluids while other minerals may be precipitated from solution or certain chemical elements from the fluid may substitute for certain other elements within a mineral. These chemical/mineralogical changes in the reservoir rocks may or may not cause volume changes, i.e., may or may not affect the permeability and porosity of the rocks. Obviously, if the mineral volume increases, it must be at the expense of open space in the rock, which caused a decrease in permeability. In locations where pressure, temperature, or rock chemistry change abruptly, minerals may be precipitated into the open spaces. This results in plugging of the plumbing system.

Silica and calcium ($CaCO_3$) are the principal minerals usually involved. The solubility of SiO_2 decreases with a decrease in temperature, with pressure changes having very little effect. SiO_2 can be precipitated into open spaces such as fractures or pores in the rock in regions where the subsurface temperature changes abruptly and at the subsurface where hot springs discharge. Calcite (calcium carbonate) has a retrograde solubility, i.e., it is more soluble at low temperatures than at high temperatures. Other carbonate species such as dolomite ($MgCO_3$), as well as sulfate species such as anhydrite ($CaSO_d$), show similar retrograde solubility relationships with temperature. In addition, the solubility of carbonate minerals decreases rapidly with a decrease in the partial pressure of carbon dioxide. Thus, as fluids that are saturated with carbonate approach the surface, carbonate minerals such as calcite are deposited as a result of the loss of CO_2, which evolves from the solution with the decrease in hydrostatic pressure.

4.1   Mineral sedimentation in geothermal waters

4.1.1   Primary geothermal fluids

Primary geothermal fluids are fluids located at the bottom of a convection cell. They may be a mixture of two or more fluid components such as meteoric and seawater and magmatic volatiles. The main types of primary fluids are Na-Cl waters, acid-sulfate waters and high salinity brines. When primary fluids rise towards the surface, they can undergo fluid phase separation and fluid mixing to form secondary geothermal fluids.

4.1.1.1 Chemical composition of primary fluids

The chemical composition of primary geothermal fluids is determined by the composition of the source fluids and reactions involving both dissolution of primary rock-forming minerals and deposition of secondary minerals, as well as by adsorption and desorption processes. The source fluids are usually meteoric water or seawater or a mixture thereof. Components of connate, magmatic and metamorphic fluids may also be present in geothermal fluids.

4.1.1.2 Na-Cl waters.

The dissolved salt in Na-Cl waters is mainly NaCl. This type of water is the most common in geothermal systems. Chloride concentrations typically range from only a few hundred to a few thousand ppm. They are lowest in waters hosted in basaltic rocks but highest in fluids which have interacted with sedimentary rocks containing evaporates. The salinity of geothermal fluids is determined by the availability of soluble salts. These salts may be leached from the aquifer

rock or added to the geothermal fluid by deep magmatic fluids. Alternatively, saline fluids may form through reactions between magmatic HCl and rock-forming minerals.

The concentrations of most major elements in Na-Cl waters are fixed by close approach to local equilibrium with secondary minerals if temperatures are above ~100 to 150°C. The only conservative major component in these waters is Cl. The mineral-solution equilibrium constrain ion activity ratios and the activities of neutral aqueous species other than Cl-bearing species, including reactive gases like CO_2, H_2S and H_2, which may be largely of magmatic origin. Some systems closely approach redo equilibrium while others significantly depart from it.

The concentrations of many trace elements (e.g., Ag, Fe, Cu, Pb, Zn) in Na-Cl geothermal waters are clearly controlled by sulfide mineral deposition. These elements typically form cautions in solution. Trace elements that form large simple anions or oxy-anions in solution may have high mobility and even show incompatible behavior (Br, I, As, Mo, W).

4.1.1.3 Acid-sulfate waters.

Deep acid-sulfate fluids have been encountered in many volcanic geothermal systems, particularly in association with andesitic volcanoes. Acidity is caused by HCl or HSO_4 or both, and evidence indicates that it mostly forms by transfer of HCl and SO_2 from the magmatic heat source to the circulating fluid.

When measured at 25°C, the pH of flashed acid-sulfate water collected at the wellhead may be as low as 2. The pH of the water is near neutral at the high temperature in the aquifer, however. Production of acidity upon cooling is related to the increased acid strength of HSO_4 with decreasing temperature. The most important difference between the Na-Cl and acid-sulfate waters is that the main pH buffer of the former is CO_2/HCO_3, but HSO_4/SO_4 in the latter. Compared to Na-Cl waters, acid SO_4-Cl waters contain higher concentrations of SO_4 and some minor elements, such as Fe and Mg, which are contained in minerals with pH-dependent solubility.

Elevated Cl concentrations (up to 120 ppm by weight) have been measured in superheated vapor. The Cl in the vapor is transported as HCl. A high Cl concentration in the vapor is due to evaporation of brine. The Cl concentration of the vapor is affected by the pH of the brine and the temperature of separation of vapor and brine.

4.1.1.4 High salinity waters

Geothermal brines can form in several ways. Brine-forming processes include dissolution of evaporates by water of meteoric origin and reaction between some primary minerals of volcanic rocks and magmatic HCl. Connate hot water brines have been encountered in sedimentary basins (White 1965). Brines may form by fluid phase separation through cooling and depressurization of moderately saline geothermal fluids in which case they are secondary.

Many metals (Ag, Au, Cu, Mo, Pb, Sn, W, Zn) form complexes with Cl−, HS− and OH− at magmatic temperatures that partition into the magmatic fluid during crystallization. As this fluid escapes from the melt into the country rock, these metals together with magmatic gases are transported into the geothermal fluid. Mixing of the magmatic and geothermal fluids and their subsequent interaction with rock-forming minerals leads to brine formation, if the magma is rich in HCl. Cooling and transformation of magmatic SO_2 into H_2S leads to precipitation of metallic sulfides. Porphyry ore-deposits are considered to form in this way.

4.1.2 Secondary fluids

4.1.2.1 Steam-heated acid sulfate waters.

In many high-temperature geothermal fields, surface manifestations consist mostly of steam vents (fumaroles), steam-heated surface water and hot intensely altered ground. Condensation of H_2S-bearing steam by heat loss or mixing with surface water and oxidation of the H_2S leads to the formation of native sulfur, thiosulfate, various polysulfides and ultimately sulfate. Steam-heated acid-sulfate waters are characterized by low Cl and relatively high sulfate concentrations. It is not uncommon that the pH is <1. At low pH, these waters often contain many metals (e.g., Al, Fe, Mn, Cr) in high concentrations. The acid water effectively dissolves the primary minerals of common volcanic rocks leaving a residue rich in amorphous silica, anatase, native sulfur, sulfides, aluminous sulfates and steatite or kaolinite.

4.1.2.2 Carbon-dioxide waters.

Thermal and non-thermal waters rich in carbonate carbon are widespread on a global scale. They are particularly common in areas of volcanic activity, but are also found in seismically active zones devoid of volcanic activity. Further, CO_2-waters occur at the boundaries of volcanic geothermal systems and around active volcanoes. Carbon-dioxide emissions from active geothermal systems and active volcanoes are largely diffuse and not confined to fumaroles and hot spring emissions. Some CO_2-waters form by mixing of mantle-derived, magmatic or metamorphic CO_2 with ground or surface waters. In volcanic geothermal systems, CO_2-waters may form by condensation of CO_2-containing vapor in perched aquifers or by mixing of downward percolating CO_2-rich condensate with the deep primary geothermal fluid. Finally, CO_2-waters may form by mixing of high temperature geothermal fluid that has not undergone fluid phase separation with cool ground water.

Deuterium (D_2H) and oxygen-18 ($D_{18}O$) data indicate that the CO_2-waters are meteoric by origin. Tritium analyses suggest, at least in some instances, short residence times. The content of 14C is low due to extensive dilution by 14C-dead carbon from the deep source. CO_2-waters are often considerably mineralized because the CO_2 makes the water quite reactive by maintaining relatively low pH, thus increasing the rate of dissolution of many common primary rock-forming minerals by enhancing their degree of under saturation. The low pH may also reduce adsorption of many trace metal cautions onto iron-hydroxide or other minerals and in this way increase the mobility of these cautions.

4.1.2.3 Mixed waters.

In up-flow zones of geothermal systems ascending boiled or un-boiled water may mix with shallow ground water. Alternatively, the thermal fluid that mixes with the cooler ground water may be two-phase (liquid and vapor). Mixed geothermal waters have been studied with the aim of assessing the temperature of the hot water component in the mixed water, largely for geothermal exploration purposes.

Variably diluted (mixed) geothermal fluids in a particular field can be identified by a negative correlation between temperature and flow rates of springs. A positive correlation between the concentrations of conservative chemical and isotopic components is also typical of mixed waters. Mixing affects the state of equilibrium between the fluid phase and both primary and hydrothermal minerals and leads to changes in the initial concentrations of reactive components in the mixed water, particularly if the hot fluid component is un-boiled water or two-phase fluid.

These changes typically involve an increase in Ca and Mg concentrations and a decrease of Na/K ratios.

4.1.3 Chemical constituents of geothermal fluids

The chemical composition of geothermal fluids is extremely variable. The chemistry of the fluid discharged is largely dependent on the geochemistry of the reservoir, and the operating conditions used for power generation and vary from one geothermal field to another. For example, fluids from the Salton Sea field (USA), which is hosted by evaporate deposits, are highly saline ([Cl] = 155 000 ppm) while those of the Krafla field (Iceland) are of low salinity ([Cl] = < 25 ppm). Chloride (Cl) is the major anion in most geothermal waters, at least if the salinity is relatively high.

Most high temperature geothermal water may contain high concentrations of at least one of the following toxic chemicals: aluminum (Al), boron (B), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and sometimes fluoride (F). The fluid concentrations of these components are largely controlled by their supply to the fluid. It is thus not surprising to have high concentrations of these components in geothermal fluids, which can extract the constituents from either the enclosing rock or degassing magma heat source.

High concentrations of trace metals are associated with high-temperature brines such as at Salton Sea in California and on the island of Nisyros, Greece. Arsenic associated with geothermal waters has been reported in several parts of the world, including hot springs from parts of the USA, Japan, New Zealand, Chile, Iceland, Kamchatka, France and Dominica.

High boron concentrations have also been found in many geothermal systems. For examples it was discovered that the high temperature reservoir in the Achuapan geothermal field in El Salvador contained highly saline water with potentially harmful minerals like B and As. The field produced wet steam and the disposal of waste geothermal water represented a major problem.

4.2. CORROSION AND SCALING

The word corrosion means the destruction of a material by chemical or electrochemical action of the surrounding environment. It is well known that iron and ordinary unalloyed steels corrode easily into rust. The most common case of corrosion is wet corrosion. The corrosive processes are very complex and take place in widely differing conditions (Hayashi, 1988).

The corrosive effects of a geothermal fluid on metals depend upon the chemical composition of that fluid. Geothermal waters have a wide range in composition, from strongly acidic waters containing sulfur and halogen acids which actively corrode most common alloys, to the more usual neutral-pH or slightly alkaline-pH waters, which may lay down protective scales of calcite, silica or metal oxides.

Contamination of geothermal fluids with oxygen (by aeration) drastically accelerates the surface corrosion of most alloys (Janik, 1985). Produced geothermal waters, not free of oxygen, may have been changed so as to lose dissolved gases, lose precipitated minerals or add atmospheric gases. The loss of dissolved gases is usually beneficial from a corrosion standpoint since the loss of carbon dioxide will tend to raise the *pH* in many geothermal waters. Corrosive attack on steel is reduced as the *pH* rises. Atmospheric gases can dissolve in the geothermal water if it is exposed to the atmosphere. The only gas of any corrosive consequence is oxygen. Although the

solubility of oxygen decreases to a minimum as the temperature rises near 100°C, it is very important to exclude oxygen contact with geothermal water (Kindle et all., 1984).

Most geothermal waters are at least mildly corrosive to iron but some will severely attack it and even affect more resistant metals. Water is likely to undergo change in chemical equilibrium when it is released or withdrawn from depth, and this may result in mineral deposition.

4.2.1. Types of corrosion

Generally speaking, we can find all the different types of corrosion in geothermal equipment and it appears useful to recall the main characteristics of each.

Uniform or ***general corrosion*** is a general all-over attack on the metal surface that is transformed into rust. Uniform corrosion is often promoted by chloride or hydrogen ions. This type of corrosion is not of great concern because the lifetime of equipment can be accurately estimated on the basis of simple tests.

Pitting is a localized form of attack in which pits develop in the metal surface. Pitting is often associated with the breakdown of a passivation film or surface scale. High concentrations of chloride and hydrogen ions stimulate the dissolution of most metals. For the initiation of the pitting corrosion the rate of metal dissolution needs to be momentarily high at one particular point.

Crevice corrosion is similar to pitting in that it is a localized attack. It occurs in crevices of equipment or under scale deposits. Contact between metal and nonmetal surfaces can cause crevice corrosion. Deposits such as corrosion products and scale deposits may produce crevice corrosion. As corrosion proceeds, oxygen within the crevice is consumed. Both chloride and hydrogen ions accelerate the dissolution of iron.

Stress corrosion cracking (SCC) is a type of failure promoted by a combination of the action of specific chemicals, such as chloride ion and tensile stress. The presence of oxygen and increased temperatures increases the severity of attack. This is the most dangerous form of corrosion in geothermal environments. The most common agents that cause stress corrosion cracking are hydrogen sulfide and chloride. Aqueous solutions containing large amounts of hydrogen sulfide cause a form of stress corrosion cracking in 1818 steel at low *pH,* especially below *pH* 4. Stress corrosion cracking caused by hydrogen sulfide is trance crystalline. This form of corrosion takes place primarily at low temperatures. At higher temperatures the solubility of hydrogen sulfide in water decreases in open systems.

Sulfide stress cracking is a form of corrosion that may occur due to tensile stress and environments involving hydrogen sulfide in an aqueous phase. Low *pH* greatly accelerates material failure. Hydrogen blistering which may occur in low strength steels exposed to waters containing hydrogen sulfide is similar. Sulfide stress cracking decreases in severity with increased temperature.

Other types of corrosion include: *galvanic* corrosion, corrosion *fatigue* and *exfoliation*, which involves the formation of layers of corrosion products, but these are less important in geothermal system.

Compared to clogging, corrosion is less of a problem for wells and open loop system. Still, and under certain unfavorable conditions corrosion potential has to be considered in the design. The types of corrosion that may take place and the components that may be corroded are:

Components sensitive for corrosion are:

- Steel casings
- Screens
- Heat Exchangers

Screens that are made of stainless steel will have a long life time and will not be very sensitive for either general thinning or pitting corrosion. However, in this case the bimetallic type of corrosion may in rare cases corrode parts of the screen, especially in areas where the screen is in contact or close to the casing.

The most sensitive component would be the steel casing. Normally, the casing is made of carbon steel and has threaded or welded joints. These joints are also the most sensitive parts that commonly will have corrosion attacks caused by the pitting type of corrosion.

Water quality factors that increase the corrosion potential are preferably a low pH, a high content of salts, and dissolved gases like oxygen and hydrogen sulfite. The corrosion potential will also increase at turbulent flow and stagnant water conditions.

Corrosion prevention. To avoid corrosion problems the first choice would be to choose as noble material as technically and economically possible, and not to mix materials with different electrochemical potential.

Corrosion problems can be limited by:

- Using corrosion resistant material, such as plastics and/or more noble metals/alloys
- Not mixing materials with different electro chemical potential
- Using cathode protection for wells with car-bon steel casing

Other protection methods would be to use coated casing and pipes. This is done by a thin plastic or epoxy layer on the inside of the metal pipes. However, such films are sensible for mechanical damages and fits badly together with threads (or welding). Damages will, if they occur, lead to serious pitting corrosion attacks. It is therefore recommended not to use coated protections, especially not for well components, that are easily damaged during construction.

4.2.2. Scaling

Depending upon its specific chemistry, water can promote scaling, corrosion or both. Water is a universal solvent, since almost everything is soluble in it to some extent. Scaling, according to the Water Quality Association, is the number one water quality issue in the US. Scale can be formed from a variety of dissolved chemical species but two reliable indicators are hardness and alkalinity. Calcium carbonate is the most common form of scale deposition attributable to groundwater.

Scaling results in dissolved materials that separate from solution, sometimes remaining suspended as small particles or attaching to a solid surface such as a pipe wall. Silica, a sand-like material, is the most common substance that scales out. Other common materials include metallic carbonates and sulfides.

Total hardness is primarily a measure of the calcium and magnesium salts in water. In addition, other minor contributing components to hardness can be aluminum, manganese, iron and zinc (Carrier, 1965). Two types of hardness are generally recognized: carbonate (sometimes referred to as temporary hardness) and non-carbonate hardness. Carbonate hardness, depending upon the nature of the water is composed of calcium or magnesium carbonates and bicarbonates. It is this

form of hardness that contributes most to scale formation. Non-carbonate hardness is normally a small component of the total hardness and is characterized by much higher solubility. As a result its role in scale formation is generally negligible.

Table 4.2.1. Water Hardness Classification (Carrier, 1965)

Hardness (as ppm $CaCO_3$)[1]	Classification
<15	Very soft
15 to 50	Soft
50 to 100	Medium hard
100 to 200	Hard
>200	Very Hard

[1]Hardness is sometimes expressed in units of grains per gallon (gpg). To convert gpg to ppm as $CaCO_3$ multiply by 17.1.

Water hardness is classified according to somewhat subjective criteria that vary from reference to reference. Table 4.2.1 provides a common interpretation. Scaling problems typically occur above levels of 100 ppm hardness.

Calcium hardness is a key parameter in evaluating scale formation. It generally constitutes 70% or more of the total hardness in water. For worst case evaluations or in the absence of sufficient information, calcium hardness can be considered equal to total hardness. If a calcium ion value is available from a water chemistry analysis, calcium hardness (as $CaCO_3$) can be calculated by multiplying the calcium ion value by 2.5.

Alkalinity is a measure of water's ability to neutralize acid. Like hardness it is usually expressed as ppm $CaCO_3$. In the range of normal groundwater chemistry, alkalinity is the result primarily of the bicarbonate content of the water. At pH values of greater than 8.3 carbonate and hydroxide can also contribute to alkalinity. Two measures of alkalinity are of interest: Methyl Orange ("M" alkalinity or total alkalinity) and Phenolphtalien ("P"alkalinity). Since P alkalinity measures that portion of the alkalinity effective at very high pH, the M alkalinity is the value of interest in evaluating scale potential.

In order to evaluate the general character (scale forming or corrosive) of a particular water sample it is necessary to know the total dissolved solids (TDS), pH and temperature in addition to the calcium hardness and the M alkalinity.

Total dissolved solids are a general indication of the quality of a water source. As TDS increases water quality problems are more likely to occur. Whether these problems are on the corrosion or scaling end of the spectrum is dependent upon other indicators.

The pH value of most ground waters is in the range of 5.0 on the acid end of the spectrum to 9.0 on the alkaline end. Scaling problems are common at pH value above 7.5.

Fig.4.2.1. Scaling

Scaling can be induced by temperature and pH changes. When flashing a liquid to produce steam in separators, the carbon dioxide (CO_2) originally dissolved in the geothermal liquid is naturally emitted in limited amounts. This creates a positive feedback loop, because the pH increases as a result of the CO_2 emission, which results in further scaling of dissolved liquids.

Scaling can be dealt with in a variety of ways. A developer can reduce the heat captured from the geothermal liquid (thereby reducing plant efficiency), add scaling inhibitors, or acidify the geothermal liquid to maintain minerals in solution. More complex equipment may be required to clean the geothermal liquid and control mineral precipitation.

Calcium carbonate precipitates can form in geothermal waters by the combination of calcium ions with carbonate ions. The calcite scales form very rapidly once the thermodynamic

conditions are correct. For practical purposes the calcite kinetics can be assumed to be instantaneous. The loss of carbon dioxide and the associated *pH* increase are the principal causes for calcite precipitation. Calcite solubility decreases as the temperature increases from 25 to l00°C and the solubility product continues to decrease up to 25O"C. However, the presence of carbon dioxide at moderate to high pressure in a geothermal reservoir enhances its solubility.

The three major classes of geothermal scales are generally considered to be

a) silica and silicates;
b) carbonate of calcium and iron;
c) sulfides of iron and heavy metals.

When geothermal waters are discharged from springs or geothermal wells, chemical reactions and evaporation occur with changes in temperature and pressure, and suspended materials are formed by chemical reactions and microorganism activity. At the time of discharge, geothermal water is saturated with chemical components due to degassing, concentration may take place by evaporation and chemical reactions, and finally material is removed from the geothermal water by deposition.

A small change in the concentration of a component can translate into a sizeable deposition rate in a geothermal well of high output. For example, a loss of 1 ppm of calcite from solution in a 20 cm diameter well producing 100 tons of water per hour, would give a deposit about 2 mm thick per day over 1 m length of pipe. Practically, deposition rates can be much greater than this. In severe scaling situations complete plugging of wells has occurred in a matter of days (Shimada, 1987).

Deposits of calcium carbonate can be readily dissolved and precipitated by water in a variety of conditions. Simple contact of water with air will expose the calcium to varying concentrations of carbon dioxide. The result of this combination is a potential precipitate that can adhere to surfaces and form a scale at some point in the water cycle (Cowan and Weintritt, 1976).

Deposition of calcium and iron carbonates can also be caused by electrochemical corrosion. The relation of corrosion to scaling is indicated by the fact that moderately corrosive waters saturated with calcite are known to have scaled steel well parts, whereas similar deposition did not occur when non-corrodible plastic filter pipes were used (Clarke and Barnes, 1969).

Calcium carbonate scaling may be *prevented* by

a) acting on carbon dioxide partial pressure;
b) acting on the *pH* of the solution and;
c) using chemical additives (scale inhibitors).

4.3. MINERAL RECOVERY

Geothermal fluids contain significant concentrations of potentially valuable mineral resources. Although their mineral content was often considered more a nuisance than an asset, there is now increasing interest in improving the economics of geothermal energy by co-producing and marketing some of the dissolved constituents. Simple cost-effective methods are needed to extract mineral byproducts from geothermal fluids. Useful methods may have already been developed in the hydrometallurgical industry that could be modified for use with geothermal fluids.

Further research and development could make the separation of minerals from geothermal water, known as mineral recovery, a viable technology. Some geothermal fluids contain significant

concentrations of dissolved minerals, while others are virtually mineral free. Mineral recovery offers several benefits, which generally fall into categories of either improving the function of the power plant (reducing scaling, allowing greater power production by lowering the injection temperature), or increasing profits (through the sale of mineral byproducts). Often a variety of benefits will result. Minerals found at geothermal power plants include zinc, silica, lithium, manganese, boron, lead, silver, antimony and strontium.

Many constituents of geothermal fluids have value provided they can be separated and purified. The recovery of a valuable material from a geothermal resource is dependent on the state and chemistry of the feedstock; the recovery may be from the fluid, or from solid material such as sludge or scale that precipitates from the fluid. The process must be economically profitable and environmentally acceptable. Previous published work on extraction of resources from geothermal fluids has focused on a wide variety of materials including precious and platinum group metals, zinc, lead, copper, manganese, rare earths, silica, lithium, arsenic, antimony, boron, bromine, iodine, strontium and barium sulfate, precipitated calcium carbonate, calcium chloride, potash, table salt, sodium sulfate, and others (Gallup, 1998; Harper et al., 1992). Most of this work has focused on extraction of silica, lithium, and zinc, the resources that have the greatest potential to be economically extracted, and on which we focus our review.

In the early history of geothermal resource development, boric acid, sulfur, and ammonium salts were recovered commercially until they lost economic competitiveness to other mining processes. (Garbato 1961; Lenzi, 1961; Villa 1975). Recently, several processes have been reported for the recovery of other valuable materials from geothermal resources (Duyvesteyn 1992; Lin et al. 2000, 2001). Typical recovery methods are discussed below.

4.3.1. Recovery from solid geothermal residues (sludge and scales)

Acid leaching: In geothermal power plants in the Salton Sea area, a solid waste separated as filter cake from the clarifier contains a mixture of iron-bearing silica, salts, and heavy metals. Hydrochloric acid has been employed to leach out the iron and other metals, such that the remaining silica becomes pure enough for uses as a pozzolanic additive for cements.

Biochemical leaching: Bioleaching used for mining low-grade copper, uranium and gold ores (Ehrlich and Brierley, 1990) has been modified to treat the solid waste separated as filter cake from the clarifiers at Salton Sea plants. In the process, acidophilic bacteria were used to leach out most of the toxic heavy metals, to make the treated solid safe for landfill disposal. In some cases the byproduct is pure enough to be used as feedstock for further processing (Premuzic et al. 1995b).

4.3.2. Recovery of metals and salts from geothermal fluids

Sorption: Synthetic ion-exchange resins as well as bacteria are known to adsorb ions selectively from solution. The selectivity and capacity of the adsorption is pH, temperature and ionic strength dependent. Laboratory studies of the use of the adsorptive property of cell walls to recover U, Co, Zn, Mn, and Li ions in solution have been reported (Premuzic et al., 1995b). However, no biological process has yet been commercialized. Separation using commercial ion-exchange resins has been used to recover zinc from high salinity brines (see Salton Sea case history below).

Evaporation: Leslie Salt operated solar evaporation ponds to recover salt minerals from saline brines at Imperial Valley, CA in the early 1970's. Evaporation is an energy intensive process that

can be employed under rare circumstances when energy costs and the need for reinjection water are of no concern. Additionally, reinjection of fluid after salt and potash removal could negatively impact the injection zone (Premuzic, 1995a).

Precipitation as sulfides: Hydrogen sulfide was added to geothermal fluids to precipitate out most heavy metals as insoluble metal sulfides (Schultze and Bauer, 1985). The advantage of this treatment is its near quantitative efficiency. However, if the geothermal brine is rich in many metals, quantitative precipitation gives rise to a complex metal sulfide mixture that requires further purification (SRI, 1980). Precipitation as hydroxides induced by raising the pH gives rise to similar problems (Hazen Research Inc., 1978).

4.3.3. Recovery of silica from geothermal fluids

Silica is a ubiquitous component of geothermal fluids and must be removed or reduced in concentration to allow other components to be removed. Most hydrothermal systems equilibrate with quartz (SiO_2) causing the fluids to have silica concentrations that reflect the temperature of the reservoir - the hotter the reservoir, the higher the silica concentration of the fluid.

During energy production, the geothermal fluid cools and some water is extracted as steam. Both processes cause the silica to become increasingly supersaturated. Eventually the silica tends to precipitate and forms scale on various plant components or in reinjection wells. Silica will also tend to precipitate on mineral extraction processing equipment if not removed prior to mineral co-production.

Fig.4.3.1. Geothermal fluid drain at Wairakey, New Zeland geothermal site. Silica precipitate of orange-brown color line the channel

There is currently world-wide interest in silica production from geothermal fluids, including work in New Zealand (Brown and Bacon, 2000), Japan (Sugita et al., 1998), Russia (Kashpura and Potapov, 2000), and the U.S. (Bourcier et al., 2001; Lin et al., 2000).

The silica is used in applications in the rubber, plastics, paper, paint, cement, ceramics, pharmaceuticals, pesticides, and adhesive industries. Some specific uses include (USGS, 1999):

- Desiccants and anti-caking agents in human and animal food,
- Abrasives in sandpaper and for use in silicon wafer polishing
- Filler in plastics, paper, paint and rubber tires
- Fiber optics and catalyst manufacturing
- Feedstock for making semiconductor silicon, fine chemicals, and chromatographic silica.

4.3.4. Recovery of lithium and alkali metals from geothermal fluids

Lithium is often enriched in geothermal fluids. Lithium is used in the production of ceramics, glass, and aluminum, and also has a growing use in rechargeable lithium batteries. Chile is the

largest lithium producer in the world, followed by Australia, China, Russia and the U.S. The U.S. has remained the leading consumer of lithium minerals and leading producer of value-added lithium products.

Lithium can be extracted from geothermal fluids by direct precipitation as lithium salts, or captured using ion exchange resins. Both methods are currently being used for commercial lithium extraction from saline (non-geothermal) brines (e.g. at Searles Lake California a dilithium sodium phosphate precipitate is made; FMC uses a proprietary ion exchange process to remove lithium from brines originating in Chile).

Both cesium and rubidium can be enriched in geothermal fluids and because of their high value could be extracted at a profit. Both are specialty chemicals that sell for a few dollars per gram. Cesium and rubidium are used interchangeably in applications in thermionics, as oxygen getters in vacuum tubes, and alloys used in photocells. The hydroxides of cesium and rubidium are the strongest known bases. Additional applications for these elements may arise given a significant cost reduction. Cesium and rubidium can be separated using high cross-linkage ion exchange resins. Novel methods utilizing crown ethers have also been investigated (Harper et al., 1992).

4.3.5. Other byproducts

Geothermal fluids could be used to produce some inexpensive salts such as $NaCl$, $Na_2SO_4.H_2O$, $CaCl_2$ and others. Although they are not of high value, they may be produced as by-products of the processes that produce other more valuable solids and may add to the profitability of geothermal co-production. Another potential by-product is high surface area precipitated calcium carbonate. Although calcium carbonate as limestone is inexpensive, freshly precipitated high surface area $CaCO_3$ has unique properties that make it useful in applications such as paper filler and allows it to command a much higher price.

Precious metals such as gold and silver are contained in geothermal scale and extraction from the scale rather than the fluid has been attempted (Gallup, 1998). Base metals such as zinc, copper, and lead are generally not highly enriched in geothermal waters. One exception is the very saline geothermal system at the Salton Sea in southern California. CalEnergy Minerals has developed a commercial zinc extraction process at this site, and has plans to remove manganese as well (see below).

Mineral recovery continues to be an issue of interest to the geothermal community. At many geothermal facilities, valuable mineral species may be available at high concentrations, but extraction of pure species tends to be difficult, expensive, and risky. For this reason, some combination of government and private sector funding is needed if this process is to occur more frequently and successfully in the U.S. Recent increases in commodity prices over the past five years make the potential economics for mineral recovery even more promising then it has been in the past.