

GEOTHERMAL TRAINING PROGRAMME Orkustofnun, Grensásvegur 9, IS-108 Reykjavík, Iceland Reports 2006 Number 5

AN EXPERIMENT ON MONOMERIC AND POLYMERIC SILICA PRECIPITATION RATES FROM SUPERSATURATED SOLUTIONS

Erlindo C. Angcoy Jr.

Technical Services Sector, Geoservices Department PNOC-Energy Development Corporation Merritt Road, Fort Bonifacio, Taguig City PHILIPPINES angcoy.ec@energy.com.ph

ABSTRACT

Experimental solutions initially supersaturated with amorphous silica were allowed to polymerize while being pumped through a column packed with silica gel. The concentrations of silica monomers and polymers in the solutions were monitored at the inlet and outlet of the column. Results of experimental runs conducted at 50°C with pure water and saline solutions (0.1 M, 0.2 M, 0.3 M and 0.4 M NaCl) showed shorter induction time and faster polymerization with increasing salinity, consistent with theory and past studies. In all runs, monomeric silica dropped to saturation for amorphous silica in the column whereas the concentration of polymerized silica changed little. A solution of 0.3 M NaCl at 90°C also showed a lesser tendency for polymeric silica than monomeric silica to precipitate on the surface of the silica gel in the packed column. However, higher temperature and salinity allowed polymers to grow large enough to deposit in the source tank. In the column, some of the polymeric silica was lost either by precipitation or filtration from solution in the void spaces of the column. The experiment demonstrated that amorphous silica scaling from geothermal brine can be mitigated by allowing dissolved silica in excess of amorphous silica solubility to polymerize, provided that factors affecting polymerization rate and polymer deposition rate are known.

1. INTRODUCTION

Harnessing geothermal energy entails overcoming the difficulties encountered in its various stages of development. Whereas geothermal projects are spurred forward after establishing the heat source and permeability, addressing problems associated with the chemical composition of the geothermal fluids is just as critical for successful exploitation. Geothermal water undergoes cooling and degassing during the process of extracting heat. These changes favour the formation of different scales along the fluid path (Arnórsson, 2004) which are often detrimental to geothermal operations. Amorphous silica is one of the major and most common scaling problems as its solubility decreases with decreasing temperatures. Depending on the conditions, amorphous silica scales may form anywhere from the production wells, surface facilities to downstream of injection wells.

Injecting the fluids back into the reservoir is either an integral part of field management and/or compliance to environmental regulations. As spent geothermal waters are injected, silica may precipitate to cause mild to severe decline in the injectivity of wells (Messer et al., 1978; Hauksson and Gudmundsson, 1986; Itoi et al., 1989; Malate and O'Sullivan, 1993; Alcober et al., 2005). High costs, both in drilling wells and treatment to restore well injectivity, make it important to maintain injection well capacities for a sustainable period. In this study, we establish potential amorphous silica scale formation in the aquifer receiving brine in the Malitbog sector of Tongonan geothermal field, Philippines with the aid of the speciation program WATCH. The scale formation, which deteriorates the injectivity of the wells, provided the motivation to investigate the precipitation rates of the different silica species in a controlled experiment.

2. BACKGROUND

The theory and mechanism of amorphous silica scaling, studies conducted in the past and their applications to address problems encountered in the geothermal industry are reviewed. As silica is the most abundant oxide in the earth's crust coupled with the need to understand its behaviour as applied to science and engineering, it is a subject of considerable study through the years. For detailed and comprehensive discussions on silica chemistry, readers are referred to Iler (1979) and Dove and Rimstidt (1994). General information on Malitbog geothermal operations and field tests in relation to the study topic is provided in this report.

2.1 Silica scaling

The term silica is a short convenient form of silicon dioxide (SiO_2) and may refer to any of its nine natural or engineered earth system forms (polymorphs). In studying geothermal fluids, the silica phases of most interest are quartz, its microcrystalline form chalcedony and amorphous silica. Quartz is the most stable and common form in nature and is invariably present as a secondary mineral of most geothermal systems. The reaction of quartz with aqueous solution can be expressed as:

$$SiO_{2,auartz} + 2H_2O \Leftrightarrow H_4SiO_{4,aaueous}$$
 (1)

In most high-temperature reservoirs, aqueous silica concentrations are controlled by quartz solubility (Fournier and Rowe, 1966). Quartz solubility is temperature dependent. Accordingly, aqueous silica concentrations in geothermal reservoirs are determined by the reservoir temperature (point 1 on Figure 1). As the reservoir water rises to the surface, it boils by depressurization and cools down and in the process it gives off heat to the steam that forms. The steam formation increases the silica concentration of the water. This causes the water become quartz supersaturated. to Experience shows, however, that quartz



FIGURE 1: Solubility curves of quartz and amorphous silica as a function of temperature: Point 1 is the silica concentration in an aquifer initially in equilibrium with quartz. During adiabatic boiling and subsequent cooling of the aquifer water, aqueous silica concentration increases and amorphous silica saturation is reached in Point 2. Further adiabatic boiling and cooling of the aquifer water will lead to supersaturation with respect to amorphous silica at Point 3

Angcoy

precipitation from supersaturated solution is very slow. Silica only precipitates at an appreciable rate if the effects of cooling and steam formation are sufficient to produce amorphous silica supersaturated solution (point 2 on Figure 1). In order to prevent the deposition of amorphous silica in geothermal installations, it is common to keep its temperature above that corresponding with saturation for amorphous silica. This limits the amount of heat that can be extracted from the fluid discharged from production wells. It is therefore also common to cool the water past the saturation levels (point 3 in Figure 1), making it supersaturated with respect to both quartz and amorphous silica. Quartz and amorphous silica solubilities have been investigated numerous times over a wide range of temperatures, pressures, and solution compositions which are summarized in the works of Chan (1989) and Gunnarsson and Arnórsson (2000).

Dissolved silica in typical conditions of geothermal reservoir waters ($<600^{\circ}$ C, 6-8 kbar) was determined by Zotov and Keppler (2002) to be of monomeric form (monosilicic acid), H₄SiO₄⁰. A monomer may also be written as Si(OH)₄⁰ showing a central Si atom with 4 separate bonded –OH, or silinol, groups. The silinol groups between two monomers form the Si-O-Si bonding into dimers, an initial step called a condensation reaction towards the formation of higher molecular weight polymers:

$$Si(OH)_4^0 + Si(OH)_4^0 \Leftrightarrow (HO)_3 Si - O - Si(OH)_3 + H_2O$$
⁽²⁾

Since Equation 2 shows no ionized species, it is alternatively written in two reactions to manifest the effects of cations and pH (Fleming, 1986):

$$H_4 SiO_4^{\ 0} \Leftrightarrow H_3 SiO_4^{\ -} + H^+ \tag{3}$$

$$H_4 SiO_4^{\ 0} + H_3 SiO_4^{\ -} \Leftrightarrow H_6 Si_2 O_7^{\ 0} + OH^{\ -} \tag{4}$$

When the monomeric concentration exceeds the amorphous silica saturation level, the growth of polymers and scale formation are functions of combined chemical and physical processes following two dominant and essentially competing pathways: (1) molecular deposition upon solid surfaces and (2) particle deposition which follows homogenous nucleation and growth of suspended particles (Weres and Apps, 1981; Klein et al., 1991). The two mechanisms compete for the supply of excess $Si(OH)_4$ in solution such that the dominant one tends to slow down the other.

Molecular deposition involves not just chemical bonding of dissolved silica directly to solid surfaces like pipe walls, forming hard, dense, difficult to remove, vitreous, and often dark-coloured scale. It also refers to the mechanism in which the growing polymer surface is a solid to which the monomer and silicate ions migrate by circulation and diffusion (heterogeneous nucleation). This mechanism is a slow process and dominant at a supersaturation ratio <2 (silica concentration/equilibrium solubility at the given condition) or at high-flow velocity such that nucleation occurs further downstream. The rate of molecular deposition of monomeric silica is a function of temperature and the density of silinol groups ionized to $-Si-O^-$ on the solid growth surface, or to an -OH group in a corroded iron. Salinity accelerates deposition by increasing the extent of surface ionization and decreasing the solubility of amorphous silica.

In particle deposition, the starting process is termed homogenous nucleation since the polymers develop spontaneously in solution. The decline of monomeric silica concentrations in solution (from initial supersaturation to saturation level) as analyzed by the molybdate method has been the principal method for studying polymerization processes. The rate of decline of monomeric silica is a strong function of initial supersaturation such that it is often instantaneous or very rapid if the ratio is >2.5 but exhibits a plateau called an induction period which can last from minutes to hours if the ratio is <2.5. The induction period and polymerization rate are subjects of many studies (summarized by Chan, 1989; Gunnarsson and Arnórsson, 2005). In general, at a given supersaturation level, induction will be shorter at a lower temperature, higher salinity, and higher pH (except in very basic solution when solubility of amorphous silica is high). The rate by which the monomers disappear to form

Angcoy

polymers (polysilicic acid) is usually expressed as (Bohlmann et al., 1980; Weres et al., 1982; Fleming, 1986):

$$-\frac{dC}{dt} = k(C - C_e)^n \tag{5}$$

where C = Monomeric silica concentration;

 C_e = Concentration corresponding to amorphous silica saturation at the reaction temperature;

k = Reaction constant;

n = Reaction order.

However, results are not consistent and reaction orders from 1 to 8 have been reported for the maximum rate at 6 < pH < 9. Others also propose different mechanisms on how the monomers polymerize leading to the development of different forms of polymerization rate equations (summary in Chan, 1989). Despite the differences, most authors agree that polymerization continues until the monomeric silica concentration falls to the solubility of amorphous silica.

Polymers continue to grow until they reach a critical size (<50 Å but sometimes down to 10-20 Å) for them to be considered colloidal particles. The colloids may deposit to a solid surface driven by transfer processes such as diffusion, flow turbulence and gravity. When the colloids are deposited along with monomeric silica (Iler, 1979), deposition rates are much faster than deposition involving monomers only, and the deposits are much denser and harder than those formed by coagulated colloids only. Simultaneous deposition of colloids and monomeric silica creates worse scaling problems than the deposition of monomeric silica only, as the depositing colloids are cemented together by the monomers (Weres and Apps, 1982). If the solution is static or flowing very slowly, the colloids may coagulate and form flocs which could either precipitate or remain suspended as a semi-solid material. In some cases, the colloids are very stable in solution and do not precipitate (Klein et al., 1991).

2.2 Previous studies and mitigating measures

Similar studies on silica chemistry have recently been carried out with objectives and methodology similar to those of the present study. Bohlmann et al. (1980) simulated geothermal brines under controlled conditions at specified supersaturation, pH, temperature and salinity and passed through columns with various substrates. They observed that once thoroughly coated with silica, the deposition behaviour was identical and independent of the type of substrate. They also observed that more than half the silica removed from solution was deposited as monomers. Polymerized silica had little tendency to deposit. Weres et al. (1982) studied experimentally and theoretically silica polymerization with the purpose of predicting its pattern under conditions typical of geothermal brines. Fleming (1986) studied condensation polymerization between monomer and silica surfaces in the absence of nucleation (seeding with colloidal amorphous silica particles of known surface area). Amorphous silica precipitation behaviour was investigated by Carroll et al. (1998). They observed slower rates in laboratory tests than in field experiments. The cause was considered to be due to chemical impurities in the geothermal brine. Gallup (1998) demonstrated that Fe and Al silicate scales were significantly less soluble than pure amorphous silica. It may require higher brine temperature to mitigate them.

Conducting local field experiments is common as results using actual geothermal brines often deviate from laboratory experiments. In their study of injection problems caused by downhole silica scaling, Nishiyama et al. (1985) observed the scale deposition was concentrated at the upstream part of the column only and that brine with high polysilicic acid concentration caused a small decrease in permeability. Axtmann and Grant-Taylor (1986) recognized that in slightly silica-supersaturated brine, monomeric silica initially deposited on growing colloidal surfaces so they concluded that it was

favourable to use a fluidized bed prior to injection. Mroczek and McDowell (1990) found that with rapidly polymerizing brine, deposition rates across gravel beds were lower compared to brine containing only monomeric silica. Mroczek et al. (2000) allowed brine with excess monomeric silica only to pass across a column packed with zirconia beads and used the results to numerically model and predict the lifetime of reinjection aquifers. The tests of Rothbaum et al. (1979) showed that deposition of polymerized silica only changed the physical appearance of the scale but had no effect on the chemical content. It was however argued that these observations were probably due to the high turbulence of the flowing brine. Dunstall and Brown (1998) and Zipfel et al. (1998) explored how hydrodynamics affect the behaviour of silica scaling.

The results of these studies helped develop other approaches to controlling silica precipitation from geothermal brines, aside from avoiding supersaturation. The exact fields utilizing the methods are widely cited in Weres and Apps (1982) and Arnórsson (2004). These include: (1) lowering the pH by acidification, (2) brine aging to convert monomeric silica to colloidal silica, (3) use of inhibitors, (4) precipitation of the silica with lime or by bubbling CO_2 through the solution, (5) mixing the brine with steam condensate and (6) removal of colloidal silica by coagulation and settling. There is no single standard solution to all silica scaling problems. Often a combination or slight modification of any of these methods has been adapted depending on the experience gained.

2.3 Operation difficulties and field tests

Malitbog is located south of the Tongonan geothermal field (Figure 2). This field forms the northern reservoir of the 1.076 km² geothermal reservation called Greater Tongonan Geothermal field in the island of Leyte, Central Philippines. Malitbog is the major outflow region of the Tongonan reservoir (Alvis-Isidro et al., 1993) and its artificial recharge by injected brine helps maintain the average well discharge enthalpies in this sector below 1,600 kJ/kg (Dacillo and Siega, 2005). All spent geothermal brine from Malitbog is injected into 3 wells (5R1D, 5R4 and As of August 2006, flow 5R7D). measurements using tracers showed that 73% of the total brine (\sim 250 kg/s) flows into wells 5R1D and 5R4 of Pad 5R1 at a temperature $\sim 160^{\circ}$ C. Most of the Malitbog brine is distributed to Pad 5R1 injection wells with a lesser flow to injection well 5R7D of Pad 5R7 to counteract the observed decline in output of the central and eastern Malitbog production wells (Herras, 2006). Thus. maintaining high injection capacities in



FIGURE 2: Map of the Greater Tongonan geothermal field, Leyte, Philippines

Pad 5R1 wells is of utmost importance not only for environmental compliance but also to achieve field management objectives.

Limited silica scale (3-8 mm/yr) forms in the surface facilities conveying the brine from the steam separators to the injection wells. Observations show decreased injectivity in wells 5R1D and 5R4 (Figures 3 and 4). The steep decline seen in Figures 3 and 4 after workover of these wells is attributed

Angcoy



to pressure build-up in a shallow two-phase permeable zone. This behaviour was initially observed in 2003 when well 5R4 acceptance improved after quenching the blow-out of well 5R12D that was eventually controlled through relief well 5R13D. Starting in March 2005, continuous quenching was done by injecting into well 5R13D a mixture of river water, main power plant condensate and brine dumped from the main brineline to Pad 5R1. However, it has been observed lately that only well 5R4 responds positively to quenching. The gradual decline is attributed to deterioration of permeability by deposition of amorphous silica in the receiving formation; but the brine injected in Pad 5R1 is slightly amorphous silica-supersaturated (oversaturation ratio of 1.1-1.2). The idea of silica deposition was substantiated when mechanical cleaning coupled with leaching by acid (HCl and HF) of the injection wells showed significant improvements in injectivity compared to mechanical cleaning alone.

Studies of silica scaling in Malitbog started in 1996 by tests using a chemical inhibitor to keep polymerized silica suspended in solution (Garcia et al., 1996). The residence time from the nearest separator station to the shallowest Pad 5R1 wellbore loss zone is 23 min. Using a polymerization vessel, it was determined that the fluid onset of silica polymerization in untreated brine was 45-55 min. In 2004, the above conditions were simulated in a field test set-up that allowed brine to flow through a column packed with broken rocks. The field test set-up was used to evaluate different mitigating measures (Alcober et al., 2005; Angcoy et al., 2005) which included: (1) brine pH modification by the addition of H_2SO_4 and (2) addition of silica inhibitors. Acidification yielded clean rock formations but posed an increased risk of corrosion while the inhibitors reduced deposition by 80-85%.

3. DESCRIPTION OF WORK

3.1 Assessment of scaling in Malitbog sector

This section aims to establish the type of scales that may precipitate from Malitbog brine as it is disposed of into injection wells. The use of geochemical tools is emphasized (analyses retrieved from PNOC-EDC integrated computer databases) but data on injection wells (from Reservoir Engineering Department of PNOC-EDC) are also presented to support the results obtained from the geochemical evaluation.

3.1.1 Scaling potential evaluation

The saturation state of the geothermal fluids from Malitbog with respect to some common scaleforming minerals was assessed with the aid of the speciation program WATCH 2.3 (Arnórsson et al., 1982 and Bjarnason, 1994). The detailed background and calculation methods of the program are discussed in Arnórsson et al. (1982). In general, the program computes the chemical composition of the aquifer fluid based on the chemical analyses of water and steam samples collected at the surface. The program can also be used to compute the resulting chemical composition when a fluid is cooled conductively or by adiabatic boiling from a reference temperature. During adiabatic boiling, the geothermal fluid may undergo varying degrees of degassing. A sample of the printout of calculations from WATCH is shown in Appendix I.

Figure 5 is a simplified flow diagram of the geothermal fluid collection and injection system in Malitbog. Table shows the 1 physical characteristics of representative wells 510D 513D and (fed to Separator Stations 51 and 52, respectively) and their discharge chemistry as analyzed from samples obtained using a doublewellhead Webre separator. Starting with the known chemical composition of water and steam samples collected at the wellhead, the fluid composition was calculated at: (1)reservoir conditions taking the quartz equilibrium temperature (T_{quartz}) to represent the aquifer temperature, (2) at 10 barassuming adiabatic g



FIGURE 5: Simplified diagram of Malitbog fluid collection and injection system

flashing of the reservoir liquid, (3) at 5 bar-g assuming adiabatic flashing of the separated brine at 10 bar-g. The objective of these calculations was to see how the liquid chemistry derived at 5 bar-g compared with analytical data on samples collected at these conditions. The calculated composition was almost identical to the analytical data, demonstrating that the model used for the calculations was reliable.

The calculated liquid compositions are compared with the analyses of brine samples in Table 2 (further details in Appendices II and III). The results were obtained by assuming degassing to be 14% and 35% of maximum of geothermal fluids in separator stations 51 and 52, respectively, showing good agreement in the components, and dissolved gases (except NH₃) and pH. If the samples were not immediately acidified upon collection, some NH₃ may have escaped which could explain why the NH₃ concentrations were consistently higher in the simulation than in the actual analyses. Acidification helps keep NH₃ in the aqueous solution as it drives the reaction shown below to the right:

$$NH_{2} + H_{2}O \Leftrightarrow NH_{4}^{+} + OH^{-}$$
(5)

At each stage where the compositions of the geothermal water were calculated, the saturation index, log (Q/K), of a mineral was obtained from the activity product (Q) and solubility constant (K). A saturation index value equal to 0 represents equilibrium, <0 undersaturation and >0 supersaturation of

the mineral in the solution. As the geothermal water boils and degasses, it becomes supersaturated with respect to many hydrothermal minerals known to be present in geothermal reservoirs, such as quartz, albite and K-feldspar. However, the kinetics of their formation is very slow and poses no concern to operations. Also, the amount of metallic sulphides that precipitate as a consequence of boiling and degassing, such as pyrite, marcasite and pyrrhotite, is limited by the low concentrations of Fe and heavy metals in most geothermal waters. Thus, the troublesome scale-forming minerals are those that can form in quantity due to both fast kinetics and high availability of all their components. These minerals include amorphous silica, calcium carbonate (calcite or aragonite) and anhydrite.

		h
	510D ^a	513D °
Physical data		
Wellhead pressure (bar-g)	12.9	14.4
Sampling pressure (bar-g)	12.1	13.9
Discharge enthalpy (kJ/kg)	1,376	1,390
Water flow (kg/s)	33.50	42.60
Steam flow (kg/s)	13.70	18.00
Vapour chemistry (in mm	ole/100 m	oles)
CO ₂	251	435
H_2S	19.30	23.10
NH ₃	1.35	1.90
Не	0	0
H ₂	1.94	3.35
Ar	0.12	0.03
N_2	10.63	2.77
CH ₄	1.73	2.25
Cl	0	0
Na	2.42	1.09
Water chemistry (in mg/k	g except p	H)
pH (25°C)	6.34	6.01
Li	20.30	21.10
Na	5,105	5,225
K	994	1,114
Ca	285	223
Mg	0.14	0.13
Fe	0.18	0.33
Cl	9,074	9,232
SO_4	20.50	19.90
HCO ₃	20.20	19.70
В	159	208
NH ₃	3.06	2.34
SIO ₂	660	667
H ₂ S ⁻	3.59	6.47
CO ₂ -total	21.20	33.80

TABLE 1: Physical and chemical characteristics of selected Malitbog production wells

^a Physical data as of 9 Jan 2006, chemistry as of 19 Aug 2005, representative of 4 production wells fed to separator station 51,

^b Physical data as of 13 Jan 2006, chemistry as of 18 Aug 2005, representative of 6 production wells fed to separator station 52.

The saturation indices for amorphous silica, calcite and anhydrite in variably boiled geothermal water of wells 510D and 513D are shown in Figures 6 and 7, respectively (other production wells in Appendix IV). At aquifer



FIGURE 6: Saturation indices of Malitbog production well 510D at 14% degassing



FIGURE 7: Saturation indices of Malitbog production well 513D at 35% degassing

conditions, the waters are at saturation with respect to both anhydrite and calcite within the anticipated limit of error. but significantly amorphous silica undersaturated. The calcite saturation index curve of well 513D shows a more pronounced "hump" than well 510D due to the selection of a higher degassing coefficient used in the calculations (0.35 vs. 0.14). Cooling, either by adiabatic boiling or conduction, makes the water more undersaturated with calcite and anhydrite because of their retrograde solubility with respect to temperature, but more supersaturated with amorphous silica.

After 2^{nd} flashing at 5 bar-g, the brine of well 510D lies just within the amorphous silica saturation level while well 513D is at a slightly higher level. Due to its prograde solubility, only amorphous silica scaling is expected towards temperatures <160°C. The scaling potentials of the brine samples injected into wells 5R1D and 5R7D (Figures 8 and 9, respectively) were also evaluated using WATCH assuming their conductive cooling or heating in the receiving

	Well	5R7D	Well	5R1D
Analysis ^b	Sample ^c	Calcul. ^d	Sample ^c	Calcul. ^e
pН	6.41	6.16	6.34	6.29
В	199	204	219	228
SiO ₂	675	688	707	718
Na	5,822	5,800	5,616	5,941
K	1,239	1,180	1,166	1,209
Mg	0.05	0.13	0.12	0.13
Ca	326	325	280	340
F	NA^{f}	1.60	NA^{f}	1.51
Cl	10,632	10,668	10,379	10,578
SO ₄	27.50	22.79	26.55	24.50
Fe	0.30	0.34	0.69	0.40
CO ₂	15.40	15.88	6.94	6.41
H ₂ S	5.02	5.37	3.26	2.11
NH ₃	0.77	6.17	1.71	4.95

TABLE 2: Comparison of brine sample analyses and liquid chemistry as calculated using WATCH^a

^a Details in Appendices II and III,

^b In mg/kg except pH,

^c Total composition in water phase at 159°C,

^d Separator station 51 wells 14% degassing,

^e Separator station 52 wells 35% degassing, separator station 51 to Sep. Station 52 brine flow ratio = 22:78,

^f No analysis available.

formation. The results indicate undersaturation levels of the minerals in the brine injected at 5R1D at temperature ranges of about 160°-250°C, and in brine injected at 5R7D at 160°-200°C. Above these temperature ranges, anhydrite or calcite may precipitate from the brine whereas temperatures below the ranges may lead to precipitation of amorphous silica in the formation.

29



3.1.2 Data on injection wells

Injection well 5R1D was directionally drilled and completed on 1 August 1982 to a total depth of 952.2 m MD (measured depth from casing head flange). It intersected the Mamban formation, which is a thick sequence of predominantly biotite-bearing hornblende-pyroxene andesite lavas, hyaloclastites and tuff breccias (Delfin et al., 1995). Petrologic analysis of the rock formations showed the Mamban formation to be volcanic breccia intensely altered to quartz + drusy anhydrite + opaques + smectite + vermiculite + illite + chalcopyrite (Alcober et al., 2005). Originally targeted as a deep well, continued drilling was not possible due to complete loss of circulation at shallower depth (Sarmiento, 1986). The well had one of the highest original injectivities in the field, estimated at 192 l/s-MPa. During its last mechanical cleaning with acid stimulation in 2004, all obstructions cleared were below the production casing shoe and within the sections of the perforated liner (565-601 m MD, 815-857 m MD). In 2000, mechanical cleaning of well 5R1D resulted in minimal capacity recovery

(from 98 to 123 kg/s) whereas acidizing registered significant improvements (from 44 to 137 kg/s in 2002 and from 9.8 to 89.9 kg/s in 2004). Again, two years after its last cleaning, it now has a capacity of 6 kg/s only. Figure 10 shows that at its major and minor permeable zones (553-658 m MD and 767 m MD, respectively) the temperature in 2001 was between 158° and 165°C, favourable to the precipitation of amorphous silica only.

Well 5R4 was vertically drilled and completed on 25 April 1980 to a total depth of 2,342 m (all vertical depths from casing head flange). It was initially tested as a producer and eventually turned into an injector in 1996. Its open section starts at 999.9 m intersecting the Mamban formation, but its minor and major permeable zones (1.900-2,000 m and 2,140-2,320 m, respectively) intersect the Mahiao sedimentary complex, which is described as sedimentary а breccia/conglomerate containing fragments of altered microdiorite, quartz monzodiorite, and minor volcanics. Within the conglomeratic unit, minor interbeds of sandstone, siltstone and claystone exist and these interbeds usually mark the contact of Mahiao sedimentary complex with the Mamban formation (Caranto and Jara, 2006). Figure 11 shows that starting at 600 m depth, it has an almost isothermal temperature. At



FIGURE 11: Temperature and pressure profiles of injection well 5R4

Angcoy

this temperature, scaling of amorphous silica, calcite or anyhdrite is not expected. But in March 1999, blockage was tagged at 2,224 m using a 3" Go-Devil tool, which is within its major permeable zone. It is possible, however, that the scales were formed when it was still used as a production well. The encouraging results of mechanical cleaning with acidizing in 5R1D was duplicated in 5R4 in 2001, increasing capacity from 76 to 201 kg/s and suggesting that acid-soluble scales in near-wellbore formation are decreasing its injectivity.

Lower downhole temperatures in 5R1D may possibly explain the more frequent decline in injectivity due to amorphous silica deposition (Figure 3). Logging of well 5R4 conducted on June 1996 and June 2001 indicated casing discontinuities in the cased-off sections of ~300-350 m and ~550-580 m. These levels were also intersected during the blow-out of 5R12D in 2003 and eventually were targeted by relief well 5R13D to quench the shallow two-phase high-pressure zone. Since March 2005, cold fluids have been injected into 5R13D to maintain quenching. These casing breaks were probably the breakthrough of cold fluids to 5R4, thus generating a positive response to quenching. However, this may also lower its downhole temperature to promote amorphous silica supersaturation since a gradual decline in its injectivity is still observed at quenched conditions (Figure 4).

3.2 Silica experiment

In view of the results from the preceding section, an experiment was conducted to provide useful information on amorphous silica scaling in Malitbog. The objective of the experiment was to obtain data on relative precipitation rates of monomeric versus polymeric silica from amorphous silica supersaturated solution. Two sets of experiments were carried out. The first set was conducted at fixed temperature (50°C), atmospheric pressure, initial silica concentration (500 mg/kg) and pH of 6-7, but salinity was varied by adding 5 M NaCl solution to the initial test solution (0 M, 0.1 M, 0.2 M, 0.3 M and 0.4 M). The second set of experiments was conducted at 90°C, atmospheric pressure, initial silica concentration of 500 mg/kg, 0.3 M NaCl and pH of 6-7. This second experiment simulates well conditions at Malitbog.

3.2.1 Experimental design

The experimental runs were performed using an oven set at the experimental temperature (Figure 12). The silica-supersaturated solution was pumped from a container across a column packed with washed silica gel. The solution was pumped against gravity to prevent channelling in the column. Pumping across the column from an experimental solution was continuous for at least 30 minutes before sampling the discharge. The same column was used in other experimental solutions. After the column, a three-way valve was manipulated to direct the outlet solution either for sampling or for pH measurement. The solution did not come into contact with any glass material in order to prevent leaching of silica. Residence time in the column was fixed by regularly monitoring the flow rate at 1 The determination of residence time ml/min. was conducted using an inert visual tracer after





completing all experimental runs. The initial and final weights of the dried column were measured.

The procedures in preparing the solutions and reagents were taken from another silica polymerization experiment (Gunnarsson and Arnórsson, 2005). Silica stock solution was prepared by dissolving silica gel in 0.1 N NaOH and filtered using 0.2 μ m cellulose acetate filter paper at room temperature. In all runs, 1 litre of experimental solution with a target concentration of 500 mg/kg SiO₂ was prepared by diluting the stock solution with deionised water and adding variable amounts of 5 M NaCl solution depending on the desired ionic strength. The experimental solution after these steps was very basic (pH \approx 11). At this pH, all silica species present in the solution were molybdate active and undersaturated with respect to amorphous silica. The undersaturated solution was kept inside the oven at the experimental temperature for at least 12 hours.

The pH of the thermally stabilized experimental solution was lowered to a target value of 6.97 by adding concentrated HCl to oversaturate it with respect to amorphous silica. Prior to acidification, the experimental solution was buffered with TRIS, $(HOCH_2)_3CNH_2$, to stabilize its pH. Polymerization of the silica-supersaturated solution proceeded in the source tank as the solution was pumped across the column. The solutions at the inlet and outlet of the column were monitored for active molybdate and total silica concentrations to determine the relative amount of monomeric and polymeric silica in the solution.

3.2.2 Sampling and analytical methods

The sample from the column inlet was extracted from the experimental solution container using a 10 ml syringe while the sample at the column outlet was collected into a small vial after passing it through a 0.2 μ m cellulose acetate filter. For analysis of monomeric silica concentration, the samples were immediately brought to room temperature through a cooling spiral and aliquots were drawn using a pipette. The entire sampling procedure was completed in less than 30 seconds to minimize the effect of cooling to polymerization. For analysis of total dissolved silica, all samples were diluted at least 10 times and acidified with concentrated HNO₃. In the first set of experiments, all samples were passed through 0.2 μ m cellulose acetate filter while in the second set of experiments a run was conducted where filtered samples were duplicated with unfiltered ones.

Monomeric silica concentration was determined using the yellow molybdate method (Franson, 1985). The absorbance was measured at 410 nm using a Cary, 1E UV-visible spectrophotometer. In theory, the molybdic acid will react only with monomeric silica in the solution. However, since the samples in the analytical procedure were diluted to become undersaturated with respect to amorphous silica, some of the monomers forming the yellow molybdosilicic complex may have also been formed from the breakdown of silica dimers and trimers (Iler, 1979). Thus, in this study, all monomeric silica is referred to as molybdate active silica. Total dissolved silica concentration was measured using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Solution pH was measured with a buffer-calibrated pH meter.

3.2.3 Results

The results of the experiment are presented in Figures 13-21 and tabulated in Appendix V. After completing all the experimental runs, the retention time of the solution in the column was determined visually, using a coloured tracer, to be ~9 minutes. The first trial of the 90°C run (Figure 19) showed almost equal total and monomeric silica levels of the inlet solution with time. To determine whether the polymers grew to sizes large enough to be filtered by the 0.2 μ m cellulose acetate filter membrane or were actually depositing in the tank, the experiment was repeated and the filtered samples were duplicated with unfiltered samples (Figures 20-21). The initial and final dry weights of the column containing the silica gel did not differ significantly.





retention time, filtered samples

varying salinities, filtered samples





4. DISCUSSION

4.1 Results of experiment

The results show that monomeric silica concentrations in the solutions flowing from the column were always at the same concentration. This indicates that monomeric silica easily precipitates on the surface of the silica gel in the packed column. However, the concentration levels approached corresponded to temperatures significantly lower than the experimental temperatures. Since it is unlikely that a more stable silica polymorph other than amorphous silica precipitated in the column, the results were taken to indicate that cooling of the outlet solution occurred with the result that amorphous silica equilibration was attained at the lower temperature. The column was kept at oven temperature except during sampling of the inlet solution. Thus, it is not likely that the solution cooled across the column. Significant cooling only occurred when the sample was brought to room temperature to ensure accuracy of the volumes measured by the pipettes. Probably due to a larger

temperature difference, the monomeric silica level in the outlet solutions approached saturation of amorphous silica at lower temperatures in the 90°C runs (73°C) than in the 50°C runs (45°C).

In contrast to the monomers, the polymerized silica formed in the inlet solutions and pumped across the column had little tendency to precipitate in the column. Most of it remained in solution when pumped through the column. In the experiments at 90°C and saline solution, the analyses of the filtered samples indicated that the polymers grew to a large enough size to be filtered from solution by the 0.2 μ m cellulose acetate filter membrane (Figures 19-20), as confirmed by the analyses of the duplicate unfiltered samples. In the experiment at 90°C, analyses of unfiltered samples indicated some polymeric silica (20 mg/kg maximum) was lost either by precipitation or filtration in the void spaces of the column (Figure 21). But compared to the losses of monomeric silica across the column, the amount of polymeric silica retained in the column was significantly less.

The experiment confirms the results of previous studies that at about a constant degree of supersaturation, pH (buffered solutions) and temperature, polymerization of monomeric silica in excess of amorphous silica saturation, is a strong function of salinity. Experiments carried out at 50°C show that increasing salinity increases silica polymerization rate in the tank solution (Figure 18). The monomers polymerized about 10 times faster in the 0.3 and 0.4 M NaCl saline solutions than in pure water. Silica polymerization rate is also a strong function of supersaturation. In the 50°C run, the 0.1 M NaCl solution was inadvertently prepared with a lower supersaturation (~165 ppm) than the The effect of salinity was offset by the low level of solution in pure water (~220 ppm). supersaturation such that the two solutions exhibited almost the same induction time but more time was required to closely approach amorphous silica saturation for the 0.1 M NaCl solution (Figure 18). At the salinity of 0.3 M NaCl (50°C and 90°C), it was anticipated that increased polymerization rate due to higher temperature would also be counteracted by the higher saturation level of amorphous silica. Thus, supersaturation was increased in the 90°C, 0.3 M NaCl run by starting at a higher initial silica level to achieve a reasonable onset of polymerization of the excess monomers after about 5 hours.

The experiment demonstrated that precipitation of amorphous silica from supersaturated solutions is decreased if the monomers in excess of saturation are allowed to polymerize. However, the successful application of this method in order to mitigate silica scaling requires a balance between both the silica polymerization rate and the deposition rate. Silica polymerization is regarded as a precursor to the precipitation of silica gel (Iler, 1979). At pH~7, the growing polymers in pure water tend to repel each other because of their negatively charged surfaces. But in saline solutions, the presence of ions reduces the repulsive forces allowing the polymers to aggregate and gel (Figure 22). In the experiment, increased salinity increased both silica polymerization and deposition rates. In all saline solutions of the experiment, the total silica concentration of the inlet solutions slightly declined from the initial silica levels indicating that some polymers had grown large enough to deposit in the tank. Growth and precipitation of the silica polymers were enhanced by the presence of electrolytes in solution. Marshall (1980) observed that the nature of cations and not the anions has greater effect. The decreasing effect of cations is $Mg^{2+}>Ca^{2+}>Sr^{2+}>Li^+>Na^+$ $> K^+$ (Chan, 1989).



Figure 22: Experiment: Silica gel precipitated in the tank at 90°C, 1 atm, 0.3 M NaCl, pH~7

4.2 Relevance of experimental results to Malitbog

Amorphous silica scaling during the injection of Malitbog brine to Pad 5R1 wells is probably dominated by the deposition of both monomeric and polymeric silica. The conditions that favour the mechanism of deposition of both forms of silica are: (1) a low degree of supersaturation (not more than 1.2); (2) an induction period of about 1 hour (Alcober et al., 2005), long enough for the brine to travel away from the wellbore to the receiving aquifer in the injection well before the onset of polymerization and (3) the presence of cations that may coagulate the polymerized silica to a solid surface rather than to the colloidal particles in suspension. Monomeric silica deposition and reheating in the formation are not rapid enough to relieve the slight supersaturation of the brine and to prevent polymerization. In relatively saline waters, deposition of both monomeric and polymeric silica is relatively fast and forms hard but microporous scales (Iler, 1979) similar to that observed in the field test of Malitbog (Alcober et al., 2005). The declining maximum well injectivity achieved after workovers (Figures 3-4) suggests that the removal and dissolution of the scales is becoming more difficult, especially in areas that can no longer be accessed by acid leaching.

The method demonstrated by the experiment to mitigate amorphous silica scaling can be applied with greater confidence if (1) silica polymerization is very fast so that no induction period is observed and (2) the conditions allow the polymers not to precipitate or, if precipitated, remain suspended in solution. To retain the maximum 300 kg/s of Malitbog brine for about 1 hour, in order to polymerize the silica in the brine prior to injection, requires an impractically large volume (~1,000 m³). At the surface, rapid polymerization of the brine is possible by increasing the level of oversaturation by either brine flashing to low pressure or rapid cooling. Either way, it opens opportunities to cascade the energy of Malitbog brine for further utilization. If cooling the Malitbog brine is not an option due to an adverse impact on field management, heterogeneous nucleation may be induced by seeding or brine transit through fluidized or packed beds, with the objective of stripping the excess silica monomers from the solution before injecting the brine.

4.3 Future work

The experimental procedure needs to be improved so as to allow direct sampling and analyses of samples without cooling. Analyses of monomeric silica concentrations may also be carried out using the more sensitive blue molybdate method. After these improvements, silica polymerization and deposition rates may be investigated with more confidence at various conditions. Laboratory tests need to be confirmed by field tests to validate the results. For instance, since the silica polymers in Malitbog brine are likely to precipitate by gravity due to a high ionic strength of the brine (\sim 0.3), field tests will help gauge the increased risk of deposition. Polymerization and deposition rates may further be complicated by the influence of trace amounts of iron, aluminium and manganese in the brine (Gallup, 1998; Yokoyama et al., 1989).

5. SUMMARY AND CONCLUSIONS

Potential amorphous silica scale formation in the aquifer receiving brine in the Malitbog sector of Tongonan geothermal field, Philippines was established with the aid of the speciation program WATCH. A laboratory experiment showed that polymeric silica has lesser tendency than monomeric silica to precipitate from the solution in a column packed with silica gel. Thus allowing the monomers in excess of the amorphous silica saturation level to polymerize before injection will possibly mitigate the declining injectivity of wells. Successful application of this method should consider the conditions that will allow deposition of polymeric silica precipitated due to dissolved salts in the solution.

ACKNOWLEDGEMENTS

This project was made possible through the fellowship granted by the government of Iceland and the United Nations University Geothermal Training Programme under the dedicated and esteemed staff of Dr. Ingvar B. Fridleifsson (Director), Mr. Lúdvík S. Georgsson (Deputy Director), Mrs. Gudrún Bjarnadóttir and Ms. Thórhildur Ísberg. The author sincerely acknowledges the critical guidance and support of Dr. Stefán Arnórsson and Ingvi Gunnarsson, both at the Institute of Earth Sciences, University of Iceland, and the PNOC-EDC management and colleagues from the Technical Services Sector who were instrumental in contributing constructive comments and the necessary data in their simple but invaluable ways.

REFERENCES

Alcober, E.H., Candelaria, M.N.R., Mejorada, A.V., and Cabel Jr., A.C., 2005: Mitigation of silica deposition in wellbore formation in Malitbog sector, Tongonan Leyte, Philippines. *Proceedings of the World Geothermal Congress 2005, Antalya, Turkey,* CD, 7 pp.

Alvis-Isidro, R.R.A., Solana, R.R., D'Amore, F., Nuti, S., and Gonfiantini, R., 1993: Hydrology of the Greater Tongonan geothermal system, Philippines, as deduced from geochemical and isotopic data. *Geothermics, 22,* 435–450.

Angcoy Jr., E.C., Alcober, E.H., Mejorada, A.V.M., Gonzalez, R.C., Cabel Jr., A.C., Magpantay, R.P., Ruaya, J.R., and Stapleton, M., 2005: Test results of another silica scale inhibitor for Malitbog geothermal brine, Tongonan, Leyte. *Geothermal Resources Council, Transactions, 29*, 681-685.

Arnórsson, S., 2004: Environmental impact of geothermal energy utilization. In: Giere, R., and Stille, P. (editors), *Energy, waste, and the environment: a geochemical perspective.* Geological Society of London, Special publications 236, 297-336.

Arnórsson, S., Sigurdsson, S., and Svavarsson, H., 1982: The chemistry of geothermal waters in Iceland. I. Calculations of aqueous speciation from 0° to 370°C. *Geochim. Cosmochim. Acta, 46*, 1513-1532.

Axtmann, R.C., and Grant-Taylor, D., 1986: Desilication of geothermal waste waters in fluidized beds. *Geothermics*, 15, 185-191.

Bjarnason, J.Ö., 1994: The speciation program WATCH, version 2.1. Orkustofnun, Reykjavík, 7 pp.

Bohlmann, E.G., Mesmer, R.E., and Berlinski, P., 1980: Kinetics of silica deposition from simulated geothermal brines. *Soc. of Pet. Eng. Journal*, 20, 239-248.

Caranto, J.A, and Jara, M.P., 2006: Factors controlling reservoir permeability at the Leyte Geothermal Production Field, Tongonan, Philippines. *Proceedings of the 27th PNOC-EDC Geothermal Conference, Makati City, Philippines*, 107-112.

Carroll, S., Mroczek, E., Alai, M., and Ebert, M., 1998: Amorphous silica precipitation (60° to 120°C): comparison of laboratory and field rates. *Geochim. Cosmochim. Acta*, 62, 1379-1396.

Chan, S., 1989: A review on solubility and polymerization of silica. Geothermics, 18, 49-56.

Dacillo, D.B., and Siega, F.L., 2005: Geochemical assessment on the sustainability of the deep geothermal resource of Tongonan Geothermal field (Leyte, Philippines). *Proceedings of the World Geothermal Congress 2005, Antalya, Turkey*, CD, 7 pp.

Angcoy

Delfin Jr., F.G., Maneja, F.C., Layugan, D.B., and Zaide-Delfin, M.C., 1995: *Stratigraphic and geophysical constraints on injection targets in the Greater Tongonan Geothermal field*. PNOC-EDC internal report.

Dove, P.M., and Rimstidt J.D., 1994: Silica-water interactions. In: Heaney, P.J., Prewitt, C.T., and Gibbs, G.V. (editors) and Ribbe, P.H. (series editor), *Silica: physical behavior, geochemistry and materials applications*. Mineralogical Society of America, Reviews in Mineralogy, 29, 259-308.

Dunstall, M.G., and Brown, K.L., 1998: Silica scaling under controlled hydrodynamic conditions: vertical flat plate and vertical cylinder tests. *Proceedings of the 23rd Workshop on Geothermal Reservoir Engineering, Stanford, California*, 204-210.

Fleming, B.A., 1986: Kinetics of reaction between silicic acid and amorphous silica surfaces in NaCl solutions. *J. Colloid and Interface Science, 110*, 40-64.

Fournier, R.O., and Rowe, J.J., 1966: Estimation of underground temperatures from silica content of water from hot springs and wet-steam wells. *Am. J. Sci.* 264, 685–697.

Franson, M. A., 1985: *Standard Methods. For the examination of waste and wastewater* (16th edition). American Public Health Association, 1268 pp.

Gallup, D.L., 1998: Aluminum silicate scale formation and inhibition (2): scale solubilities and laboratory and field inhibition tests. *Geothermics*, 27, 485-501.

Garcia, S.E., Candelaria, M.N.R., Baltazar Jr., A.D.J., Solis, R.P., Cabel Jr., A.C., Nogara, J.B., Reyes, R.L., and Jordan, O.T., 1996: Methods of coping with silica deposition – the PNOC experience. *Proceedings of the 18th PNOC-EDC Geothermal Conference, Manila, Philippines*, 93-110.

Gunnarsson, I. and Arnórsson S., 2000: Amorphous silica solubility and the thermodynamic properties of $H_4SiO_4^{\circ}$ in the range of 0° to 350°C at P_{sat} . *Geochim. Cosmochim. Acta, 64*, 2295-2307.

Gunnarsson, I. and Arnórsson S., 2005: Impact of silica scaling on the efficiency of heat extraction from high-temperature geothermal fluids. *Geothermics*, *34*, 320-329.

Hauksson, T., and Gudmundsson, J.S., 1986: Silica deposition during injection in Svartsengi field. *Geothermal Resources Council, Transactions, 10*, 377-383.

Herras, E.B., 2006: *Mahanagdong – Malitbog – South Sambaloran 2006 first quarter reservoir geochemistry report*. PNOC-EDC internal report, 33 pp.

Iler, R.K., 1979: *The chemistry of silica: solubility, polymerization, colloid and surface properties, and biochemistry.* John Wiley and Sons, New York, 866 pp.

Itoi, R., Fukuda, M., Jinno, K., Hirowatari, K., Shinohara, N., and Tomita, T., 1989: Long-term experiments of waste water injection in the Otake geothermal field, Japan. *Geothermics*, *18*, 153-159.

Klein, C.W., Iwata, S., Takeuchi, R. and Naka, T., 1991: Prediction and prevention of silica scaling at low levels of oversaturation: case studies, and calculations for Unenotai geothermal field, Akita Prefecture, Japan. *Proceedings of the 16th Workshop on Geothermal Reservoir Engineering, Stanford, California*, 165-176.

Malate, R.C.M., and O'Sullivan, M.J., 1993: Mathematical modelling of silica deposition in Tongonan-1 reinjection wells, Philippines. *Geothermics, 22,* 467-478.

Marshall, W.L., 1980: Amorphous silica solubilities-III. Activity coefficient relations and predictions of solubility behavior in salt solutions, 0-350°C. *Geochim. Cosmochim. Acta, 44*, 925-931.

Messer, P.H., Pye, D.S., and Gallus, J.P., 1978: Injectivity restoration of a hot-brine geothermal injection well. *J. Petroleum Technology*, *30*, 1225-1230.

Mroczek, E.K., and McDowell, G., 1990: Silica scaling field experiments. *Geothermal Resources Council, Transactions, 14-II*, 1619-1625.

Mroczek, E.K., White, S.P., and Graham, D.J., 2000: Deposition of amorphous silica in porous packed beds- predicting the lifetime of reinjection aquifers. *Geothermics*, 29, 737-757.

Nishiyama, E., Hirowatari, K., and Kusunoki, K., 1985: Study in injecting low temperature geothermal brine. *Geothermal Resources Council, Transactions, 9- II*, 347-351.

Rothbaum, H.P., Anderton, B.H., Harrison, R.F., Rohde, A.G., and Slatter, A., 1979: Effect of silica polymerisation and pH on geothermal scaling. *Geothermics*, *8*, 1-20.

Sarmiento, Z.F., 1986: Waste water reinjection at Tongonan geothermal field: results and implications. *Geothermics*, 15, 295-308.

Weres, O., and Apps, J.A., 1981: Kinetics of silica polymerization. J. Colloid and Interface Science, 84-2, 379-402.

Weres, O., and Apps, J.A., 1982: Prediction of chemical problems in the reinjection of geothermal brines. *Geological Society of America, Special Paper 189*, 407-426.

Weres, O., Yee, A., and Tsao, L., 1982: Equations and types of curves for predicting the polymerization of amorphous silica in geothermal brines. *Soc. of Pet. Eng. Journal, 22*, 9-16.

Yokoyama, T., Takahashi, Y., Yamanaka, C., and Tarutani, T., 1989: Effect of aluminium on the polymerization of silicic acid in aqueous solution and the deposition of silica. *Geothermics*, *18*, 321-325.

Zipfel, H.A., Dunstall, M.G., and Brown, K.L., 1998: Investigations of the onset of silica scaling around circular cylinders. *Proceedings of the 20th New Zealand Geothermal Workshop, Auckland, NZ*, 341-346.

Zotov, N., and Keppler, H., 2002: Silica speciation in aqueous fluids at high pressures and high temperatures. *Chemical Geology*, 184, 71-82.

APPENDIX I: Sample of WATCH print-out to determine scaling potential of Malitbog production wells

ICELANDI	C WATER CHEMIST	RY GROUP		Program WATCH, version 2.	3 / 2004
STEP 1: C	alculation of aqu	ifer condit	ions from steam	and water samples.	
Malitbog produ	ction well 510D				
Water samp	le (mg/kg)	Steam s	ample		
pH/deg.C	6.34/25.6	Gas (vo	lume %)	Reference temperature deg.C	: 267.1 (Quartz)
CO2	21.20	CO2	0.00		
H2S	3.59	H2S	0.00	Sampling pressure bar abs.	: 13.1
NH3	3.06	NH3	0.00	Discharge enthalpy kJ/kg	: 1171. (Calculated)
В	159.0000	H2	13.57	Discharge kg/s	: 47.2
SiO2	660.00	02	0.00	Steam fraction at collection	: 0.1797
Na	5105.00	CH4	12.09		
K	994.00	N2	74.33	Measured temperature deg.C	
Mg	0.140			i C	
Ca	285.00	Liters g	as per kg		
F	1.340	condens	ate/deg.C 0.19/25.0	Condensate (mg/kg)	

Cl	9074.00				pH/deg.C		0.00/ 0.0			
SO4	20.50	Total stear	m (mg/kg)		CO2		0.00			
Al	0.0000	CO2	6131.92		H2S		0.00			
Fe	0.1800	H2S	365.11		NH3		0.00			
IDS	0.00	NH3	12.76		Na		0.00			
Ionic strength =	0.26580									
Ionic balance :	Cations (mol.eq.) =	0.26106104		Anions (m	ol.eq.) = 0	25596878		Difference	v(%) = 1.9	7
Liquid phase comp	oonents (mg/kg)				Vapor pha	use (mg/kg)		Gas pressu	ires (bar-ab	s.)
В	130.4218	CO2	1119.52		CO2		0.00	CO2	0.213E+0	1
SiO2	541.37	H2S	68.57		H2S		0.00	H2S	0.652E-01	
Na	4187.44	NH3	4.80		NH3		0.00	NH3	0.823E-03	
K	815.34	H2	0.39		H2		0.00	H2	0.635E-01	
Mg	0.115	02	0.00		02		0.00	O2	0.506E-36	
Ca	233.77	CH4	2.77		CH4		0.00	CH4	0.462E-01	
F	1.099	N2	29.72		N2		0.00	N2	0.465E+00	0
Cl	7443.06				H2O		0.526E+02	2		
SO4	16.82				Total		0.554E+02	2		
Al	0.0000									
Fe	0.1476									
TDS	0.00 Aquifer	steam fractio	n = 0.0000							
Ionic strength =	0.19629				1000/T (K	(elvin) = 1	.85			
Ionic balance :	Cations (mol.eq.) =	0.19268577	Anions (m	ol.eq.) = 0.	18851227		Difference	e(%) = 2.1	9	
Oxidation potentia	l (volts) : Eh H2S	=-0.424 Eh	CH4= -0.49	98 Eh H2=	-0.496 E	h NH3 = -0.	487			
~										
Chemical geothern	nometers (degrees C	C)								
Quartz 267.1 (Fournier & Potter, 1	1982)								
Chalcedony 254.3	(Fournier, 1977)									
Na/K 273.0 (Arnorsson et al., 19	83)								
Activity coefficien	its in water									
H+	0.650	K+		0.489		FeSO4+		0.557		
OH-	0.508	Ca++		0.120		FeCl++		0.099		
H3SiO4-	0.525	Mg++		0.163		FeCl2+		0.557		
H2SiO4	0.107	CaHCO3+	F	0.585		FeCl4-		0.525		
H2BO3-	0.469	MgHCO3	+	0.525		FeCl+		0.525		
HCO3-	0.525	CaOH+		0.585		Al+++		0.022		
CO3	0.088	MgOH+		0.597		AlOH++		0.107		
HS-	0.508	NH4+		0.469		Al(OH)2+		0.568		
S	0.099	Fe++		0.120		Al(OH)4-		0.542		
HSO4-	0.542	Fe+++		0.022		AlSO4+		0.542		
SO4	0.078	FeOH+		0.557		Al(SO4)2-		0.542		
NaSO4-	0.568	Fe(OH)3-		0.557		AlF++		0.107		
KSO4-	0.568	Fe(OH)4-	_	0.099		AlF2+		0.568		
F-	0.508	Fe(OH)++	-	0.099		AlF4-		0.542		
Cl-	0.489	Fe(OH)2+	-	0.568		AlF5		0.088		
Na+	0.525	Fe(OH)4-		0.568		A1F6		0.004		
		- (())								
Chemical species i	in water - ppm and le	og mole						Water pH	is 5.223	
H+	0.01	-5.037	Mg++		0.11		-5.336	Fe(OH)3	0.15	-5.865
OH-	0.05	-5.503	NaCl		1193.30		-1.690	Fe(OH)4-	0.00	-8.238
H4SiO4	865.66	-2.045	KCl		103.91		-2.856	FeCl+	0.03	-6.518
H3SiO4-	0.17	-5.745	NaSO4-		3.58		-4.521	FeCl2	0.00	-8.852
H2SiO4	0.00	-11.412	KSO4-		3.91		-4.539	FeCl++	0.00	-15.288
NaH3SiO4	0.19	-5.804	CaSO4		4.65		-4.467	FeCl2+	0.00	-16.157
H3BO3	745.78	-1.919	MgSO4		0.01		-7.200	FeCl3	0.00	-17.439
H2BO3-	0.19	-5.505	CaCO3		0.01		-6.953	FeCl4-	0.00	-18.695
H2CO3	1560.09	-1.599	MgCO3		0.00		-11.306	FeSO4	0.00	-9.956
HCO3-	6.83	-3 951	CaHCO3+		17 73		-3 756	FeSO4+	0.00	-17 701
CO3	0.00	-9342	MgHCO3+		0.00		-7 928	A1+++	0.00	0.000
H2S	68.02	-2 700	CaOH+		0.00		-6.068	AIOH++	0.00	0.000
HS-	0.53	_4 704	MoOH+		0.00		-7 450		0.00	0.000
S	0.00	-13 713	NH40H		5 53		-3.802	AI(OH)2	0.00	0.000
U2804	0.00	-13./13	NU4.		2.55		2 004		0.00	0.000
112504	1.00	-10.609	18114⊤ Eo⊥⊥		∠.∠ 4 0.01		-3.900	AI(OH)4-	0.00	0.000
11504-	1.03	-4./19	FCTT Fall		0.01		-7.040	A1004+	0.00	0.000
504 UE	0.03	-4.202	re+++		0.00		-20.242	AI(SO4)2-	0.00	0.000
Пľ Е	0.03	-4.502	reOH+		0.00		-8.839	AIF ⁺⁺	0.00	0.000
r-	0.50	-4.5/9	re(OH)2		0.00		-10.091	AIF2+	0.00	0.000
U-	0009.78	-0.726	Fe(OH)3-		0.00		-16./14	AIF3	0.00	0.000
Na+	3717.27	-0.791	Fe(OH)4		0.00		-19.877	AIF4-	0.00	0.000
K+	759.72	-1.712	Fe(OH)++		0.00		-12.709	AlF5	0.00	0.000

Ca++	225.34	-2.250	Fe(OH)2+	0.08		-6.057	AlF6	0.00	0.000
Logarithms of m	ineral solubility p	roduct constants	(K) and ion activity	y products (Q)	in water				
	log K	log Q		log K	log Q			log K	log Q
Adularia	-14.372	99.999	Albite, low	-13.938	99.999	Analcim	e	-11.563	99.999
Anhydrite	-8.425	-8.479	Calcite	-13.219	-13.566	Chalcedo	ony	-1.928	-2.045
Mg-Chlorite	-86.296	99.999	Fluorite	-11.052	-12.916	Goethite		3.237	-2.686
Laumontite	-24.709	99.999	Microcline	-14.998	99.999	Magnetit	e	-15.258	-24.927
Ca-Montmor.	-72.582	99.999	K-Montmor.	-33.869	99.999	Mg-Mon	tmor.	-74.087	99.999
Na-Montmor.	-34.152	99.999	Muscovite	-17.838	99.999	Prehnite		-37.927	99.999
Pyrrhotite	-11.288	-52.071	Pyrite	-29.035	-55.697	Quartz		-2.046	-2.045
Wairakite	-24.894	99.999	Wollastonite	7.203	5.231	Zoisite		-38.758	99.999
Epidote	-38.383	99.999	Marcasite	-12.809	-55.697	Talc		8.084	4.786
Chrysotile	14.233	8.877	Sil. amorph.	-1.612	-2.045				

STEP 2: Calculation of brine composition from 1st separator vessel (10 bar-g).

Aquifer liquid bo	oiled to 184.0 °C			Degassing coefficient is 0.1400					
Liquid phase con	nponents (mg/kg)			Vapor ph	ase (mg/kg	 ()	Gas pres	sures (bar-a	 bs.)
B	162.0251	CO2	76.42	CO2	5424.24	~	CO2	0.244E-0	1
SiO2	672.56	H2S	13.04	H2S	297.77		H2S	0.173E-0	2
Na	5202.13	NH3	5.43	NH3	2.22		NH3	0.258E-0	4
K	1012.91	H2	0.00	H2	1 99		H2	0 195E-0	3
Mσ	0 143	02	0.00	02	0.00		02	0.000E+0	0
Ca	290.42	CH4	0.03	CH4	14 08		CH4	0.174E-0	3
F	1 365	N2	0.16	N2	151.60		N2	0.107E-0	2
I Cl	0246.64	112	0.10	112	151.07		H2O	0.107E-0	$\frac{2}{12}$
504	20.80						Total	0.110E+()2
304 A1	20.89						Total	0.110E+0)2
AI E-	0.0000								
TDC	0.1654	quifar staam frastia	-0.1051						
1D5	0.00 A	iquiter steam maction	1- 0.1931						
Ionic strength	= 0.26041				1000/T (Kelvin) = 2	2.19		
Ionic balance	: Cations (mol.ec	(1.) = 0.25576815	Anions (mol.eq.)	= 0.25057867			Differen	ce(%) = 2.0	05
Oxidation pot	ential (volts) : E	Eh H2S= -0.379 Eh	CH4= -0.419 Eł	n H2= -0.398	Eh NH3= -	0.447			
Chemical geo Quartz 299 Chalcedony 2 Na/K 271	thermometers (deg 0.2 (Fournier & P 280.5 (Fournier, 1 .2 (Arnorsson et	grees C) otter, 1982) 1977) al., 1983)							
Activity coeff	icients in water								
H+	0.691	K+	0 542		FeSO4+		0.606		
OH-	0.560	Ca++	0.173		FeCl++		0.147		
H3SiO4	0.500	Ma++	0.175		$F_{e}C12+$		0.147		
H28:04	0.158		0.224		FaC14		0.000		
H2DO2	0.138	MallCO2-	0.032		FeCl4-		0.577		
112603-	0.522	CoOLL	0.377				0.377		
CO2	0.377		0.052				0.045		
105	0.134	MgOn+	0.043				0.138		
н5-	0.560	NH4+	0.522		AI(OH)2	.+	0.017		
S	0.14/	Fe++	0.1/3		AI(OH)4	-	0.592		
HSO4-	0.592	Fe+++	0.045		AISO4+		0.592		
SO4	0.120	FeOH+	0.606		AI(SO4)	2-	0.592		
NaSO4-	0.617	Fe(OH)3-	0.606		AIF++		0.158		
KSO4-	0.617	Fe(OH)4	0.147		AIF2+		0.617		
F-	0.560	Fe(OH)++	0.147		AlF4-		0.592		
Cl-	0.542	Fe(OH)2+	0.617		AlF5		0.134		
Na+	0.577	Fe(OH)4-	0.617		AlF6		0.011		
Aquifer liquid bo	oiled to 184.0 °C				Degassir	ng coefficien	nt is 0.1400) :	
Chemical spec	cies in water - ppn	n and log mole					Water pl	H is 5.813	
H+	0.00	-5.652	Mg++	0.14	-5.241	Fe(OH)3		0.00	-7.703
OH-	0.09	-5.291	NaCl	603.24	-1.986	Fe(OH)4-		0.00	-9.393
H4SiO4	1071.81	-1.953	KCl	44.10	-3.228	FeCl+		0.18	-5.702
H3SiO4-	1.96	-4.687	NaSO4-	4.60	-4.413	FeCl2		0.00	-11.660
H2SiO4	0.00	-9.346	KSO4-	3.09	-4.641	FeCl++		0.00	-16.731
NaH3SiO4	2.50	-4.674	CaSO4	4.10	-4.521	FeCl2+		0.00	-17.431
H3BO3	925.45	-1.825	MgSO4	0.01	-6.981	FeCl3		0.00	-18.809
H2BO3-	1.27	-4.680	CaCO3	0.03	-6.478	FeCl4-		0.00	-20.330
H2CO3	90.32	-2.837	MgCO3	0.00	-10.406	FeSO4		0.00	-8.699
HCO3-	10.64	-3.758	CaHCO3+	10.68	-3.976	FeSO4+		0.00	-18.828

Angcoy

CO3	0.00	-7.878	MgHCO3+	0.00	-7.951	Al+++	0.00	0.000
H2S	11.13	-3.486	CaOH+	0.04	-6.176	AlOH++	0.00	0.000
HS-	1.86	-4.250	MgOH+	0.00	-8.060	Al(OH)2+	0.00	0.000
S	0.00	-13.209	NH4OH	2.84	-4.092	Al(OH)3	0.00	0.000
H2SO4	0.00	-13.357	NH4+	4.29	-3.624	Al(OH)4-	0.00	0.000
HSO4-	0.07	-6.174	Fe++	0.07	-5.899	AlSO4+	0.00	0.000
SO4	12.02	-3.903	Fe+++	0.00	-20.049	Al(SO4)2-	0.00	0.000
HF	0.06	-5.538	FeOH+	0.00	-8.284	AlF++	0.00	0.000
F-	1.31	-4.161	Fe(OH)2	0.00	-9.548	AlF2+	0.00	0.000
Cl-	8859.67	-0.602	Fe(OH)3-	0.00	-15.680	AlF3	0.00	0.000
Na+	4963.44	-0.666	Fe(OH)4	0.00	-19.534	AlF4-	0.00	0.000
K+	988.89	-1.597	Fe(OH)++	0.00	-13.614	AlF5	0.00	0.000
Ca++	284.94	-2.148	Fe(OH)2+	0.00	-8.155	AlF6	0.00	0.000
Logarithms of mi	neral solubility product	t constants	(K) and ion activity pro	oducts (O) i	n water			
0	log K	log Q	()	log K	log Q		log K	log Q
Adularia	-14.997	99.999	Albite, low	-14.468	99.999	Analcime	-11.767	99.999
Anhydrite	-6.931	-7.732	Calcite	-11.151	-11.661	Chalcedony	-2.298	-1.953
Mg-Chlorite	-80.977	99.999	Fluorite	-10.657	-11.735	Goethite	-1.126	-4.060
Laumontite	-24.766	99.999	Microcline	-15.900	99.999	Magnetite	-22.950	-25.866
Ca-Montmor.	-74.047	99.999	K-Montmor.	-35.138	99.999	Mg-Montmor.	-75.470	99.999
Na-Montmor.	-35.349	99.999	Muscovite	-18.265	99.999	Prehnite	-35.894	99.999
Pyrrhotite	-56.973	-70.121	Pyrite	-87.795	-78.512	Quartz	-2.454	-1.953
Wairakite	-23.824	99.999	Wollastonite	8.710	6.764	Zoisite	-35.810	99.999
Epidote	-37.856	99.999	Marcasite	-68.613	-78.512	Talc	11.224	9.395
Chrysotile	18.114	13.301	Sil. amorph.	-1.858	-1.953			

APPENDIX II: Data for calculation of mixed brine in separator stations 51 and 52 at 10 bar-g

TABLE 1: Determination of brine mixture chemistry from 1st separator vessel of separator station 51

	Unit	W501	W508D	W510D	W511D	Composition at 1 st separator
Mass flow at	kg/s	41.2	38.6	47.2	51.8	
wellhead pressure						
First separator ves	sel brine	(10 bar-g	g, 184°C) ^a	1		
Water flow	kg/s	33.95	31.86	37.99	41.33	145.13
pH (at 184°C)	_	6.01	5.51	5.81	5.42	5.67
В	mg/kg	203	160	162	239	193
SiO ₂	mg/kg	616	613	673	694	652
Na	mg/kg	5,793	4,809	5,202	6,048	5,495
Κ	mg/kg	1,197	1,023	1,013	1,224	1118
Mg	mg/kg	0.12	0.10	0.14	0.10	0.12
Ca	mg/kg	376	246	290	315	308
F	mg/kg	1.64	1.70	1.37	1.44	1.52
Cl	mg/kg	10,805	8,728	9,247	11,389	10,107
SO_4	mg/kg	23.33	20.77	20.89	21.45	21.59
Fe	mg/kg	0.44	0.34	0.18	0.33	0.32
CO_2	mg/kg	60.3	75.76	76.42	162.03	96.88
H_2S	mg/kg	9.78	11.5	13.04	20.63	14.10
NH ₃	mg/kg	3.81	5.3	5.43	8.82	5.99
H ₃ SiO ₄ ⁻	moles	3.0×10 ⁻⁵	9.2×10 ⁻⁶	2.1×10 ⁻⁵	8.8×10 ⁻⁶	1.7×10^{-5}
$H_2BO_3^-$	moles	4.3×10 ⁻⁵	1.0×10 ⁻⁵	2.1×10 ⁻⁵	1.3×10 ⁻⁵	2.1×10 ⁻⁵
HCO ₃ ⁻	moles	2.0×10 ⁻⁴	9.2×10 ⁻⁵	1.7×10 ⁻⁴	1.7×10 ⁻⁴	1.6×10^{-4}
CO_{3}^{-2}	moles×2	5.0×10 ⁻⁸	6.7×10 ⁻⁹	2.6×10 ⁻⁸	1.1×10 ⁻⁸	2.3×10 ⁻⁸
HS ⁻	moles	6.3×10 ⁻⁵	2.6×10 ⁻⁵	5.6×10 ⁻⁵	4.0×10 ⁻⁵	4.6×10 ⁻⁵

^a Degassing at 14% was selected to calculate the composition of individual well discharges.

	Molar concentrations of anions of weak acids in brine mixture at 184°C								
pН	$H_3SiO_4^ H_2BO_3^ HCO_3^ CO_3^{-2}(\times 2)$ HS^- Sum Target Delta								
5.67	1.4×10 ⁻⁵	1.8×10^{-5}	1. 7×10 ⁻⁴	1.9×10 ⁻⁸	4.6×10 ⁻⁵	2.5×10 ⁻⁴	2.5×10 ^{-4 a}	-3.8×10 ⁻⁷	

TABLE 2: Determination of brine mixture pH from 1st separator vessel of separator station 51

^a Total moles of anions of weak acids in brine mixture.

 TABLE 3: Determination of brine mixture chemistry from 1st separator vessel of separator station 52

	Unit	W503	W509	W513D	W514D	W515D	W517	Comp. at 1 st separator
Mass flow at well	kg/s	40.70	42.00	60.60	31.80	35.10	24.70	
head pressure	-							
First separator v	essel brin	e (10 bar-	g, 184°C)	a				
Water flow	kg/s	32.35	35.18	48.43	23.38	27.81	20.52	187.67
pH (at 184°C)		6.06	5.91	5.97	5.83	5.67	6.17	5.93
В	mg/kg	220	226	215	188	247	246	223
SiO ₂	mg/kg	703	577	689	884	710	597	688
Na	mg/kg	5,069	5,825	5,401	5,459	5,588	7,307	5667
K	mg/kg	1,047	1,036	1,151	1,248	1,186	1,371	1153
Mg	mg/kg	0.05	0.19	0.13	0.15	0.15	0.14	0.13
Ca	mg/kg	189	535	231	204	228	681	326
F	mg/kg	1.64	1.28	1.39	1.47	1.35	1.25	1.40
Cl	mg/kg	8,749	10,376	9,542	9,571	9,794	13,143	9996
SO_4	mg/kg	19.43	26.25	20.57	19.55	30.91	28.25	23.68
Fe	mg/kg	0.60	0.34	0.34	0.36	0.48	0.27	0.40
CO_2	mg/kg	18.42	44.30	54.07	47.31	50.83	36.26	42.82
H_2S	mg/kg	0.75	5.81	7.03	5.96	6.46	4.61	5.24
NH ₃	mg/kg	3.33	4.74	4.76	6.68	5.75	3.08	4.71
H ₃ SiO ₄	moles	3.8×10 ⁻⁵	2.3×10^{-5}	3.0×10 ⁻⁵	2.8×10^{-5}	1.6×10^{-5}	4.4×10 ⁻⁵	2.9×10^{-5}
$H_2BO_3^-$	moles	5.0×10 ⁻⁵	3.8×10 ⁻⁵	4.0×10^{-5}	2.6×10^{-5}	2.3×10^{-5}	7.9×10 ⁻⁵	4.1×10 ⁻⁵
HCO ₃	moles	6.8×10 ⁻⁵	1.2×10^{-4}	1.7×10^{-4}	1.2×10^{-4}	8.9×10 ⁻⁵	1.5×10^{-4}	1.2×10^{-4}
CO_{3}^{-2}	moles×2	1.8×10^{-8}	2.4×10^{-8}	3.7×10^{-8}	1.5×10^{-8}	9.9×10 ⁻⁹	5.8×10 ⁻⁸	2.7×10^{-8}
HS	moles	5.1×10 ⁻⁶	3.1×10 ⁻⁵	4.1×10 ⁻⁵	2.7×10^{-5}	2.1×10 ⁻⁵	4.0×10 ⁻⁵	2.8×10^{-5}

^a Degassing at 35% was selected to calculate the composition of individual well discharges.

TABLE 4: Determination of brine mixture pH from 1st separator vessel of separator station 52

Molar concentrations of anions of weak acids in brine mixture at 184°C										
pН	$H_3SiO_4^ H_2BO_3^ HCO_3^ CO_3^{-2}(\times 2)$ HS^- Sum Target Delta									
5.93	2.81×10^{-5}	3.86×10 ⁻⁵	1.23×10 ⁻⁴	2.55×10 ⁻⁸	2.88×10 ⁻⁵	2.2×10 ⁻⁴	2.2×10^{-7} a	4.1×10 ⁻⁷		

^a Total moles of anions of weak acids in brine mixture.

APPENDIX III: Data for calculation of mixed brine from separator stations 51 and 52 at 5 bar-g

	II:4	From separator	From separator	Brine mixture
	Unit	station 51 ^a	station 52 ^b	to pad 5R1
First separa	ator vessel br	ine (5 bar-g, 159°	°C)	
Water flow	kg/s	55	190	245
pН	at 159°C	6.33	6.16	6.29^{b}
В	mg/kg	235	204	228
SiO ₂	mg/kg	726	688	718
Na	mg/kg	5,982	5,800	5,941
Κ	mg/kg	1,217	1,180	1,209
Mg	mg/kg	0.14	0.13	0.13
Ca	mg/kg	344	325.	340
F	mg/kg	1.48	1.60	1.51
Cl	mg/kg	10,551	10,668	10,578
SO_4	mg/kg	25.00	22.79	24.50
Fe	mg/kg	0.42	0.34	0.40
CO_2	mg/kg	3.67	15.88	6.41
H_2S	mg/kg	1.16	5.37	2.11
NH ₃	mg/kg	4.6	6.17	4.95
H ₃ SiO ₄ ⁻	moles	7.5×10 ⁻⁵	4.8×10 ⁻⁵	6.9×10 ⁻⁵
$H_2BO_3^-$	moles	10.6×10 ⁻⁵	6.1×10 ⁻⁵	9.6×10 ⁻⁵
HCO ₃ -	moles	2.8×10 ⁻⁵	9.5×10 ⁻⁵	4.3×10 ⁻⁵
CO_{3}^{-2}	moles×2	2.0×10 ⁻⁸	4.6×10 ⁻⁸	2.6×10 ⁻⁸
HS	moles	1.5×10^{-5}	5.4×10 ⁻⁵⁻	2.4×10^{-5}

 TABLE 1: Determination of brine mixture chemistry at 5 bar-g (injection to Pad 5R1)

^a Calculated brine mixture in Table 1, Appendix II adiabatically boiled to 5 bar-g at 14% degassing, ^b Calculated brine mixture in Table 3, Appendix II adiabatically boiled to 5 bar-g at 35% degassing.

TABLE 2: Determination of brine mixture pH at 5 bar-g (injection to Pad 5R1)

	Molar concentrations of anions of weak acids in brine mixture at 159°C							
pН	H ₃ SiO ₄	$H_2BO_3^-$	HCO ₃ ⁻	$CO_{3}^{-2}(\times 2)$	HS ⁻	Sum	Target	Delta
6.29	6.7×10 ⁻⁵	9.3×10 ⁻⁵	4.6×10 ⁻⁵	3.0×10 ⁻⁸	2.6×10 ⁻⁵	2.3×10 ⁻⁴	2.3×10 ⁻⁵ a	-1.2×10 ⁻⁵
3 - 1	1 0							

^a Total moles of anions of weak acids in brine mixture.



APPENDIX IV: Malitbog production wells scaling potential

Angcoy



APPENDIX V: Silica experiment results

TABLE 1: 50°C, pure water, 1 atm, pH~7, 9 minutes retention time, filtered samples

Inlet solution

Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	407	412	5 ^d
24	402	415	13 ^d
100	404	413	10 ^d
179	392	413	21 ^d
244	394	413	18 ^d
1,504	394	404	9 ^d
3,420	235	311 ^a	76 ^a
4,289	231	335 ^a	104 ^a
4,534	225	392	167 ^d
5,709	233	371	138 ^d
7,074	228	386	158

Outlet solution							
Time	SiO _{2, monomeric}	SiO _{2, total}	SiO _{2, polymeric}				
(min)	(mg/kg)	(mg/kg)	(mg/kg)				
11	165	175	10 ^d				
44	161	178	17 ^d				
114	159	172	13 ^d				
189	164	177	14 ^d				
254	164	178	14 ^d				
1,514	167	189	21 ^d				
3,429	164	312	147 ^b				
4,301	173	339	165 ^b				
4,534	173	341	168 ^d				
5,739	180	355	175 ^d				

 a Removed in plot due to low values,
 b Excluded in plot since no equivalent analyses from inlet,

 c Set to zero if plotted,
 d Used in inlet vs. outlet polymeric silica plots.

TABLE 2: 50°C, 0.1 M NaC	l, 1 atm.	, pH~7, 9	minutes re	tention time,	filtered sam	ples
--------------------------	-----------	-----------	------------	---------------	--------------	------

Outlet solution

1	
60	Intion
201	
	so

				Outlet solution				
Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)		Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	345	339	-6 ^{c,d}		47	165	166	1 ^d
34	348	337	-11 ^c		1,074	168	167	-1 ^{c,d}
154	344	336	-9 ^c		1,809	166	169	3 ^d
1,062	340	332	-7 ^{c,d}		2,479	171	190	19 ^d
1,791	335	340	5 ^d		3,057	167	228	61 ^b
2,445	316	326	10 ^d		3,929	174	259	85 ^b
3,057	268	282 ^a	14 ^a		4,434	166	255	89 ^b
3,897	237	257 ^a	20 ^a		5,404	172	269	97 ^b
4,389	241	274 ^a	33 ^a		5,999	171	268	97 ^d
5,329	218	299 ^a	81 ^a		6,899	172	283	110 ^b
5,924	212	311	99 ^d		7,366	166	266	100 ^b
6,844	220	282 ^a	62 ^a					
7,360	210	273 ^a	63 ^a					
8,549	204	301	97					
9,672	203	293	90					

^a Removed in plot due to low values, ^b Excluded in plot since no equivalent analyses from inlet, ^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.

ic

TABLE 3: 50°C, 0.2 M NaCl, 1 atm, pH~7, 9 minutes retention time, filtered samples

Inlet solution

Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	377	366	-11 ^c
108	379	377	-1 ^c
338	375	375	0^{d}
1,296	241	301 ^a	60 ^a
1,888	226	336	110 ^d
2,798	212	232 ^a	19 ^a
3,278	216	304 ^a	88^{a}
4,513	199	320	121 ^d

Outlet solution						
Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)			
23	164	164	0			
108	173	159	-14 ^c			
356	166	163	-4 ^{c,d}			
1,318	161	273	112 ^b			
1,908	164	296	132 ^d			
2,818	162	304	142 ^b			
3,288	159	298	140 ^b			
4,558	164	292	128 ^d			

^a Removed in plot due to low values,

^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.

TABLE 4	50°C 03	M NaCl 1	atm_nH~7	9 minutes retentio	on time	filtered s	amples
1 M D L L T.	50 C, 0.5	IVI INACI, I	aun, pri 7,) minutes retention	m unite,	mitered S	ampies

Inlet solution

Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	374	353	-21 ^c
84	370	358	-12 ^c
360	355	351	-5 ^{c,d}
1,619	213	313	100 ^d
2,688	197	303	106 ^d

Outlet solution						
Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymer} (mg/kg)			
32	157	152	-4 ^c			
472	161	164	3 ^d			
1,636	156	273	117 ^d			
2 797	165	276	110 ^d			

^a Removed in plot due to low values,

^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.

TABLE 5: 50°C, 0.4 M NaCl, 1 atm, pH~7, 9 minutes retention time, filtered samples

Inlet solution

Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	371	337	-34 ^c
69	368	336	-33 ^c
332	346	321	-25 ^{c,d}
1,605	205	306	101 ^d
2,672	197	284	87 ^d

Outlet solution

Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
47	162	151	-11 ^c
328	158	142	-16 ^{c,d}
1,672	156	268	112 ^{c,d}
2,705	156	278	122 ^{c,d}

^a Removed in plot due to low values,

^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.

Inlet solution			Outlet solution				
Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)	Time (min)	SiO _{2, monomeric} (mg/kg)	SiO _{2, total} (mg/kg)	SiO _{2, polymeric} (mg/kg)
0	489	457	-33°	37	260	256	-4 ^c
32	486	485	-1 ^c	65	261	256	-5°
58	500	487	-13°	260	277	280	4
234	476	481	5	324	268	271	3
302	461	476	15	485	271	281	10
465	473	479	6	1,200	276	262	-13 ^c
1,180	377	383	6	1,532	270	297	27
1,510	355	349	-5°	2,579	280	316	36
2,555	356	337	-20 ^c				

TABLE 6:	Experiment 1 results at 90°C, 0.3 M NaCl, 1 atm, pH~7,
	9 minutes retention time, filtered samples

^a Removed in plot due to low values,

^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.

TABLE 7:	Experiment 2 results at 90°C, 0.3 M NaCl, 1 atm, pH~7,
	9 minutes retention time, filtered samples

Outlet solution

Time (min)

30

90

396

1,116

1,272

1,538

SiO_{2, monomeric}

(mg/kg)

250

270

275

238

274

275

SiO_{2, total}

(mg/kg)

237

251

273

271

245

262

SiO_{2, polymeric}

(mg/kg) -13^c

-20^c

-3^{c,d}

33^d

-29^{c,d}

-14^c

Inlet solution

Time	SiO _{2, monomeric}	SiO _{2, total}	SiO _{2, polymeric}
(min)	(mg/kg)	(mg/kg)	(mg/kg)
0	479	446	-33°
63	492	461	-31 ^c
366	408	401	-7 ^{c,d}
1,083	345	416	71 ^d
1,261	337	401	64 ^d
1,468	336	318	-18 ^c

^a Removed in plot due to low values, ^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d- Used in inlet vs. outlet polymeric silica plots.

TABLE 8: Experiment 2 results at 90°C, 0.3 M NaCl, 1 atm, pH~7, 9 minutes retention time, unfiltered samples

Inlet solution

Time	SiO _{2, monomeric}	SiO _{2, total}	SiO _{2, polymeric}
(min)	(mg/kg)	(mg/kg)	(mg/kg)
0	479	492	13
63	492	491	-1 ^{c,d}
366	408	445	37 ^d
1,083	345	462	117 ^d
1,261	337	463	126 ^d
1 527	336	448	113 ^d

U	Jut	let	SO	lut	ion	

- ..

Time	SiO _{2, monomeric}	SiO _{2, total}	SiO _{2, polymeric}	
(mm)	(mg/kg)	(mg/kg)	(III g/Kg)	
30	250	239	-11 ⁻	
90	270	257	-14 ^{e,u}	
396	275	293	17 ^a	
1,116	238	349	110 ^a	
1,272	274	384	110 ^d	
1,538	275	389	114 ^d	

^a Removed in plot due to low values,

^b Excluded in plot since no equivalent analyses from inlet,

^c Set to zero if plotted,

^d Used in inlet vs. outlet polymeric silica plots.