METHODS OF COPING WITH SILICA DEPOSITION - THE PNOC EXPERIENCE

S. E. Garcia, M. N. R. Candelaria. A. D. J. Baltazar Jr.. R. P. Solis.
A. C. Cabel Jr., J. B. Nogara, R. L. Reyes and O.T. Jordan

PNOC-Energy Development Corporation, Memtt Rd., Fort Bonifacio. Makati, Phils.

Abstract

Several methods of coping with silica deposition from geothermal waters have been undertaken by PNOC-EDC to maximize power output from these fluids. Initially, the problem of amorphous silica deposition in surface pipelines and the reinjection wells was prevented by operating the production separators at pressures higher or equal to amorphous sllica saturation. However, increasing demands for additional power and stringent environmental controls have dictated the need to find alternative methods of coping with silica deposition. Several options have been studied and tested to be able to utilize fluids for production. These include: acid treatment, polymerization and deposition of silica in surface ponds or sumps. and chemical inhibition. As each brine is unique, methodologies used for mitigation of the silica problem have been varied.

1.0 INTRODUCTION

One of the major operational constraints in the harnessing of the full power potential of geothermal brines is the deposition of amorphous silica on surface pipelines and the well bores. Thus. one of the major thrust of operational research at PNOC-EDC is to find economical methods of controlling silica deposition in the Fluid Collection and Disposal System (FCDS) and injection wells. Several studies have been undertaken by PNOC-EDC which rely on an understanding of the kinetics of silica polymerization and the mechanisms of the deposition process.

At the deep hot reservoir, silica solubility is controlled by the quartz form. However, as the fluid reaches the surface and steam is separated from the liquid in production separators. the liquid is cooled and silica concentrations are increased. At lower temperatures, silica solubility is controlled by the amorphous form. Silica, like most chemical species has a much lower solubility upon cooling and silica scaling at different sections of the FCDS becomes a major problem for geothermal field operators like PNOC-EDC. Initially, the problem of amorphous silica deposition in surface pipelines and the reinjection wells was prevented by operating the production separators at pressures higher or equal to amorphous silica saturation.

However. in some cases like Botong where the silica concentration is very high (–1200 mg/kg), this would require unreasonably high production separation pressures (3.5 MPa). obviously, other methods of coping with silica deposition should be undertaken to be able to utilize this brine for power generation.

In other fields (e.g. Bacman I), increasing demands for electricity required the extraction of heat from the saturated brine by a secondary working fluid as in binary systems, resulting in brine oversaturated with silica. The silica deposition potential increases for these fluids and acid treatment of the brine was studied. Some production fields (e.g. Tongonan) have undergone pressure drawdown due to continued exploitation, producing highly saline and silica saturated brine at the production separators. PNOC undertook experiments looking into the possibility of using chemical inhibitors to prevent silica deposition, rather than costly mechanical cleaning of pipelines and regular workovers or acidizing of reinjection wells.

In exploration and developing fields, stringent environmental controls for the disposal of waste brine to surface water ways have limited the testing of exploration wells. Discharge testing of newly drilled wells through silencers, produces waters oversaturated with silica at the weirbox. At this stage, hot injection of discharged brine is not economically feasible, thus methods of cold injection without silica deposition were studied

This paper summarizes the PNOC-EDC experience on methods of coping with silica deposition at the different geothermal fields it operates. As each brine is unique, methodologies used for mitigation of the silica problem have been varied.

2.0 COLD INJECTION SCHEMES

Stringent environmental controls for the disposal of waste geothermal brine into surface waters has severely constrained the discharge testing of wells in exploration and development areas like MIGP and Bacman II (Botong). The only economic alternative was cold injection of waste brine into existing wells. The major constraint identified for cold injection is the high supersaturation with silica of brine flashed at the silencer weirbox, which will readily precipitate in surface pipelines and the well bore.

When the hot geothermal water is underground, silica equilibrium is controlled by *quartz* (Fournier and Rowe, 1977) at least when temperatures are above 180°C (Arnorsson, 1995). The predominant form of the dissolved silica at high temperatures is monosilic acid $Si(OH)_4$. In the course of heat extraction from geothermal fluids oversaturation with respect to *quartz* is reached but the kinetics of *quartz* deposition is very slow, or negligible under conditions of geothermal interest.

However, the form of silica normally deposited at the *surface* is amorphous silica. This is usually formed when rapidly ascending geothermal fluids are sufficiently cooled and become supersaturated with the metastable phase. Amorphous silica has no crystalline structure and its solubility (Fournier and Rowe, 1977) is given by the following equation:

$$\log Ce = 4.52 - 731/(t°C + 273.15) \quad (1)$$

Thus, silica saturation in production separators and brine lines *can* be expressed in the form:

$$SSI_{Ce} = [tSiO_2]/Ce \quad (2)$$

where $tSiO_2$ is the total silica concentration.

The deposition of amorphous silica from a supersaturated solution follows one of two possible mechanisms:

1. homogeneous formation and growth of a colloid (nucleation, ripening and growth) and its subsequent precipitation, producing low bulk density, porous; very soft, non adhesive type of deposit.
2. Direct or molecular deposition on solid surfaces to give vitreous, very hard, difficult to remove high density product, usually formed in pipelines at high concentrations of silica and temperatures.

The rate of silica deposition from amorphous silica supersaturated waters is apparently affected by several factors. These include: (1) the degree of supersaturation, (2) temperature (3) salinity, (4) pH, and (5) flow regime. It appears that temperature has a greater influence on the rate of amorphous silica deposition, than the degree of supersaturation (Arnorsson, 1995). As a rule of thumb reaction rates decrease by 2-4 orders of magnitude for every 10°C drop in temperature. It has also been observed that

precipitation occurs much more slowly from solution when the aqueous silica is in the form of polymers rather than as monomers.

Therefore, one method of controlling silica deposition is by "ageing" the brine in storage ponds or sumps where the dissolved monomeric silica is allowed to be converted to the relatively non adhesive polymeric form or colloid. The brine is allowed to dwell in a pond or sump for sufficiently long periods for practically all the monomeric silica in excess of the pseudo-equilibrium silica solubility to polymerize. The pseudo-equilibrium silica solubility Cx is defined as the solubility of silica in equilibrium with chemisorbed silicic acid and calculated by Fleming (1986) as:

$$\ln Cx = 9.74 - 2630/[1.983*(t°C + 273.15)] \quad (3)$$

It appears that in ageing ponds or sumps deposition is controlled by the excess monomeric form and is practically nil if $SSI_{Cx} \leq 1$ as defined by:

$$SSI_{Cx} = (\text{monomeric } SiO_2)/Cx \quad (4)$$

It is believed that compact or adherent gel or solid scale will not form if the silica in solution is converted into the polymerized form, with monomeric silica maintained at very low levels.. This is hinged on the mechanism that for electrostically coagulated silica colloid to be cemented together would require cementation of the particles by molecular deposition between them. This would need dissolved or monomeric silica in solution. When the colloidal silica is in equilibrium with monomeric silica this cementation is slow. The fraction of monomeric silica against total silica was monitored to deduce a practical correlation between this fraction and the type of deposit formed

The ponds or sumps are constructed such that the residence time is sufficient for the complete polymerization and possible deposition of the polymerized silica, with the injection of innocuous or silica depleted brine into the reinjection wells. If ever some of the polymerized silica does not settle in the pond it will be carried away by the brine in the metastable. weakly floculated, non-adhesive form and can be easily washed away by pumping water inside the well bore.

2.1 EXPLORATION AND DEVELOPMENT STAGE - MlGP

Discharge testing of production wells at the Mindanao 1 Geothermal Project (MlGP) has adopted the Zero Effluent Disposal Scheme (ZEDS) to meet the waste water disposal requirements of the project. This was adopted due to a need to inject all the waste fluids from discharge testing and drilling activities to prevent surface water contamination within the Mindanao 1 Geothermal Field reservation

An important aspect of this system is the cold injection scheme. Waste waters coming from wells undergoing medium-term discharge (MTD) testing are allowed to cool from initially high temperature at the twin silencer weirbox into surface ponds or sumps, before transport into a system of pipelines and open canals into deep reinjection wells.

The system is largely made up of series of concrete sumps situated near and connected to the well through cellar drains or 6" alvenius pipes. The sumps vary from 1200^{m3} to 2500 m^3 in capacity, and baffled to ensure longer water retention. The sumps from each pad are similarly interconnected with 6 alvenius pipes. This maximizes the temperature drop of the waste waters as it travels from well pad sumps towards sumps at lower elevations or close to the reinjection sector. Residence times range from one to three hours. Wells KL-1RD and KL-2RD were utilized as RI wells. Initial injection capacity of KL-1RD was at 94 kg/s, while KL-2RD was at 100 kg/s-. The schematic lay-out of the ZEDS is shown in Fig. 1.

Wells in pad A have very high water flows, which required the construction of open canals to sufficiently cool the fluids before reinjection. The canal is about one meter wide and half meter deep constructed in a cascaded manner for maximum turbulence.

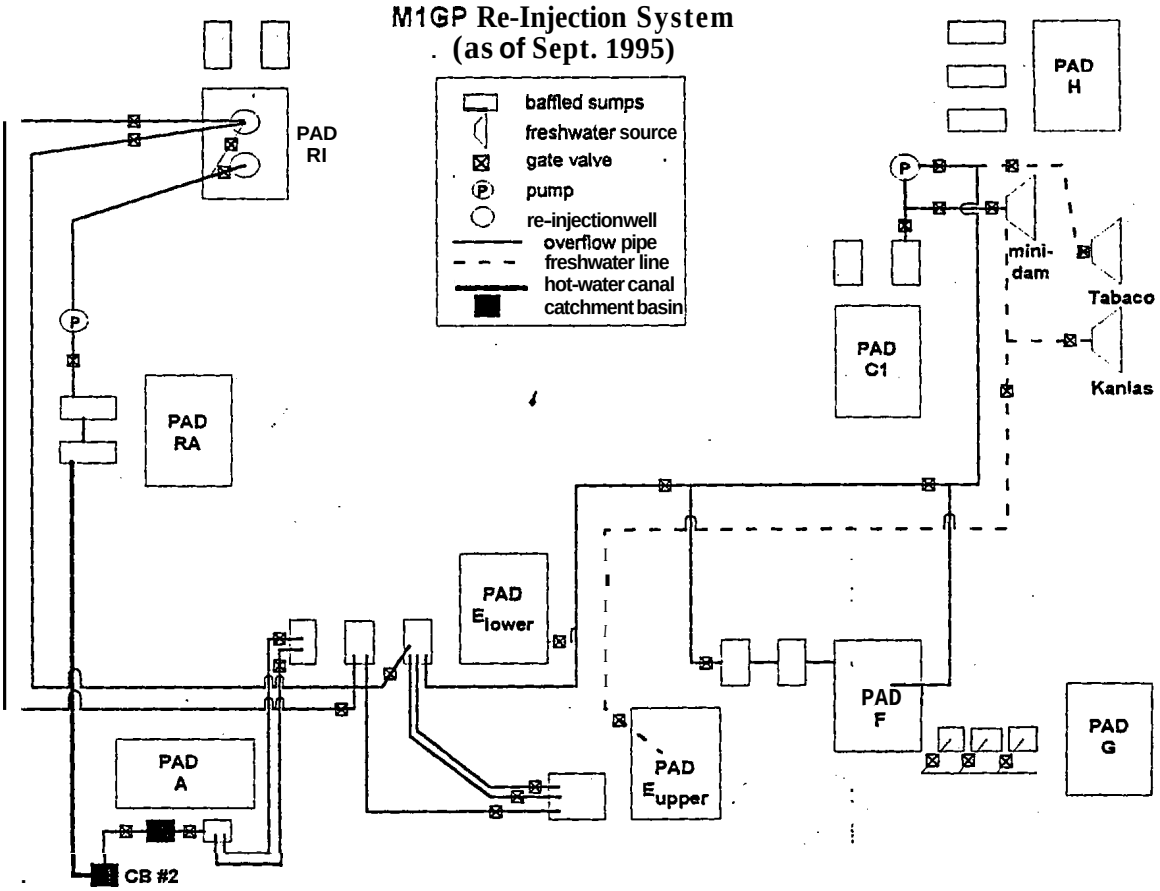


Fig.1. The MIGP Zero Effluent Disposal System.

Representatve data obtained from the silica and temperature monitoring conducted is shown in Table. 1.

Table 1. Representative silica monitoring sheet for the ZEDS. Three wells are simultaneously discharging namely SK-6D, SK-4B, SK-3D, with weirbox water flows of 35, 20 and 24 kg/s respectively.

Sampling Point	t(°C)	pH	Cl	mSiO2	tSiO2	Cx	Ce	SSICx	SSICe	mSiO2 / tSiO2
			concentration in mg/kg							
SK-3D wbx	90	6.35	7259	850	973	440	321	1.93	3.03	.87
SK4Bwbx	92	7.53	6000	608	621	449	330	1.35	1.88	.98
SK6Dwbx	89	6.52	7138	755	966	436	317	1.73	3.04	.78
Pad Eu sump	62	7.43	6310	394	644	324	218	1.21	2.95	.61
Pad El sump	58	6.73	6776	270	788	309	205	0.87	3.84	.34
CB #2	47	6.87	6845	251	740	269	172	0.93	4.29	.34
Pad RA sump2	35	6.79	6793	218	735	229	141	0.95	5.23	.30

The brine is highly oversaturated at the weirbox with typical values of SSI ranging from 2 to 3. Due to the high oversaturation, the silica is expected to polymerize upon cooling in the sumps and canals. The fraction of monomeric silica against total silica is still high (>0.80) at the weirbox, and precipitates formed at the weirbox and canals are hard scales. Monomeric silica reach minimum values close to 200 mg/kg and are undersaturated with respect to pseudo-equilibrium amorphous silica at the outlet of the Pad RA sump, which serves as the final sampling point before the brine with polymerized silica is injected The total sllica at this point is still high and only a fraction of the total silica (about 200 mg/kg) was deposited in the ZEDS. The $mSiO_2/tSiO_2$ fraction at the FSPis <0.5, and deposits observed are all soft and gelatinous in nature. In most cases, the gelatinous, fluffy precipitate formed does not settle in the sumps as the fluids are cooled but is carried by the water into the injection wells.

From January to December 1995, a total of 12 wells have successfully undergone medium term discharge testing using the ZEDS.' The duration of the MTD was from one week to two months. In addition to the discharge effluents, drilling fluids, waste water from workover and acidizing operations also found their way into the sumps of the ZEDS. Rainwater also contributed to these fluids. Daily monitoring during the utilization of the ZEDS has been confined to pH, temperature, Cl, monomeric and total silica concentrations only. In cases, where SSI_{Cx} at the Pad RA sump #2 was above 1, the wastewaters were diluted with river waters before injection. Typically this dilution is carried out when the temperature of the waste waters is lower, such that dilution will give benefit rather than lower the temperature and decrease solubility of amorphous silica. The amount of &luting fluid is calculated by balancing the effect of temperature decline and dilution effects, by simple mass and heat balance calculation with respect to silica and temperature.

In the three years that this scheme has been in effect at M1GP, no serious decline in injection capacity has been noted in wells KL-1RD and KL-2RD. The wells are still under vacuum conditions during injections. Scraper samples collected at KL-1RD showed gelatinous, fluffy silica in the well bore together with some clay materials (from drilling effluents). Perhaps the polymerized silica (or floc) was carried out by the fluids into the fractured formation sufficently far away from the well bore, for it to cause any serious injection decline. In this way, sufficient reheating of the polymerized silica in the formation *can* redissolve or increase the solubility of silica.

2.2 PALINPINON 11- NASUJI

Waste water injection in all PNOC-EDC projects became necessary in compliance with environmental regulations. During the commissioning of the 20 MWe Nasuji modular power plant last January 1994, injection wells NJ-1RD and OK-8RD were utilized as injectors. However, the waste fluid acceptance of OK-8RD declined and dropped to zero after two months of operation.. As an emergency measure, a cold water injection scheme (Fig. 2) was introduced with SG-1RD as the recipient well of the cold fluid (63°C-65°C) discharge from the Nasuji thermal pond to comply with environmental regulations.

Injection wells NJ-1RD and OK-8RD were initially accepting 129 kg/s of waste brine from the Nasuji power plant. The injection capacity of NJ-1RD and OK-8RD declined to *52* and 65 kg/s, respectively. The reduction in capacity was attributed to well communication as shown by increases in WHP whenever one of the wells was shut and the other utilized. Sodium fluorescein tracer tests confirmed this suspected communication. A casing break was formed in NJ-1RD at between 400 to 500 m during its workover. On the other hand, OK-8RD was accidentally cement plugged during work-over and was eventually abandoned

To compensate for the loss of OK-8RD, SG-1RD was commissioned to accept the excess brine (50-60 kg/s) which was initially dumped at the Nasuji thermal pond The brine was cascaded fiom the pad silencer into the pond The cooled brine is transported by gravity through 6" victualic pipes to the NJA pad and then to SG-1RD (Figs. 2 and 3).

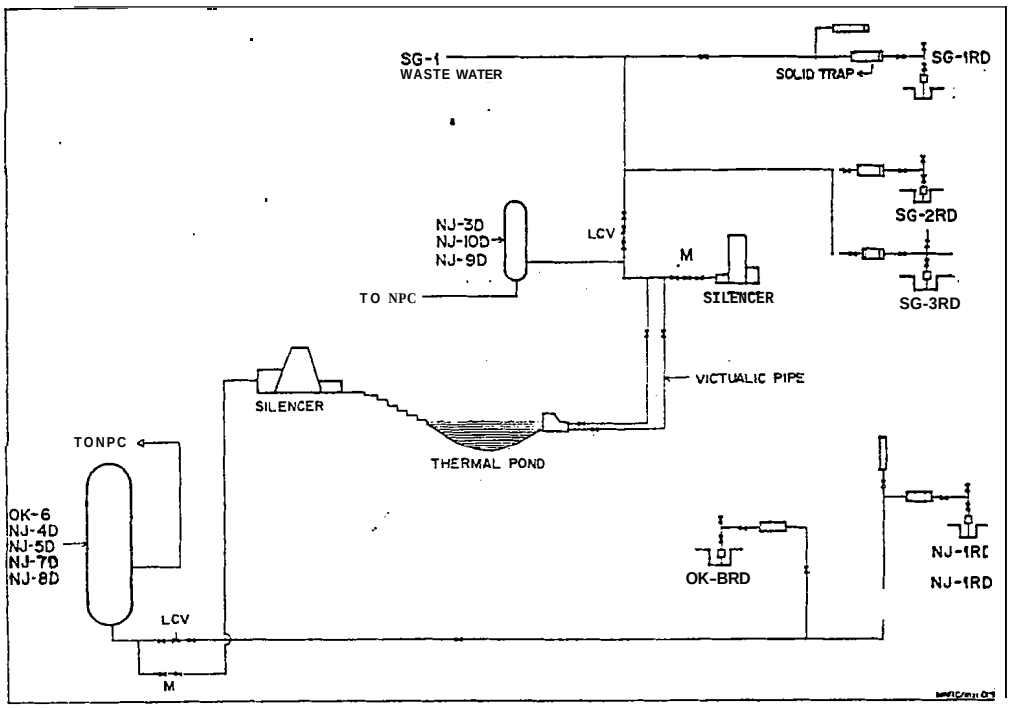


Fig. 2. Schematic layout of the Nasuji cold injection scheme.

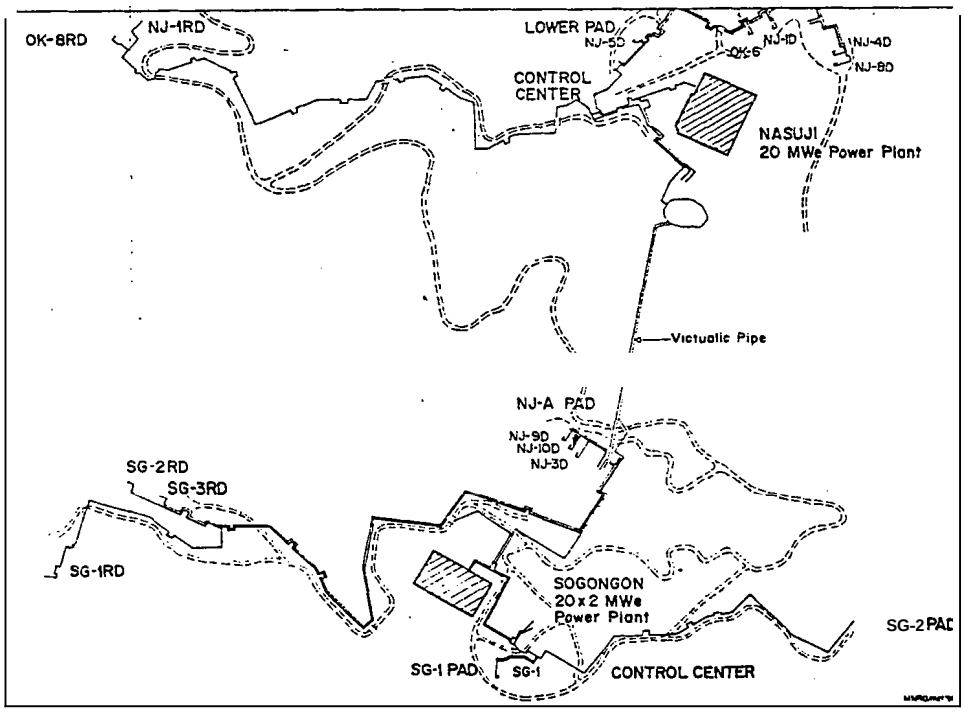


Fig.3. Plan view of the Nasuji cold injection scheme, showing the production separators, the cross country victualic lines and the reinjection well SG-1RD.

The temperature, total and monomeric silica concentrations of the brine at the inlet and outlet of the thermal pond were monitored to check for correlations with deposition. Representative chemistry is shown in Table 2.

Date	TEMP (°C)		SILICA (Inlet)		SILICA (Outlet)		SSI (Met)		SSI (Outlet)		mSiO2 / tSiO2	
	Inlet	Outlet	Total	Mono	Total	Mono	Ce	Cx	Ce	CX	Inlet	Outlet
1/5/95	95	65	836	666	908	281	2.44	1.43	2.69	0.83	0.80	0.31
1/9/95	88	65	863	515	871	273	2.75	1.19	2.58	0.81	0.60	0.31
1/16/95	90	65	860	814	864	2293	2.68		2.62	0.89	0.82	0.34
1/23/95	90	65	861	686	836	278	2.68	1.55	2.48	0.82	0.80	0.33
1/31/95	93	65	872	726	864	298	2.61	1.59	2.58	0.88	0.83	0.34

Jar test experiments on the settling potential of the polymerized silica in the Nasuji thermal pond outlet were also conducted. Total silica concentrations were taken every hour for solutions of the Nasuji cold brine from the outlet which were placed under a constant temperature water bath of 70°C. Results suggest that the colloid formed is very stable in solution and can stay suspended for more than six hours. This could even be longer, but the test was conducted only for six hours.

However, during the commissioning of the Sogongon modular power plant, cold brine from the Nasuji thermal pond (50-60 kg/s) was mixed with the hot brine from Sogongon (30-35 kg/s). The brine from the Nasuji thermal pond has completely polymerized silica or in the colloid form while the hot brine from the Sogongon module is assumed to be completely in the monomeric form. Mixing of brine rich in monomeric silica with colloidal silica is expected to promote deposition. Mroczek and Reeves (1994) found that under controlled conditions, silica scaling is maximum at fractions of monomeric silica against total silica of 0.80, while scaling was negligible at fractions of 0.5 and below. Surprisingly these mixtures produce soft deposits, and hard vitreous deposits were formed only from the fresh unpolymerized silica.

Date	SG-1 Module Hot Brine		Nasuji Cold Brine (TP Outlet)				SG-1RD		
	mSiO2	t°C	mSiO2	tSiO2	t°C	Tf	$tSiO_2$ mix	SSICe	mSiO2 / tSiO2
3/14/95	669	165	284	779	61	102	735	1.96	0.86
3120195	670	165	256	819	62	103	759	2.01	0.81
6113195	682	165	267	887	61	104	816	2.13	0.76
6/17/95	726	165	288	904	61	102	804	2.14	0.80

The mixing of cold and hot brine continued for more than six months. due to the absence of any available injection well for the Sogongon brine. In the event that the SG-1 hot brine is not injected together with the cold brine at SG-IRD, the brine had to be disposed through the river system.

After more than a year of utilization, the victualic pipes and SG-1RD solid traps were inspected to check the type of deposits formed. Vitreous, soft and hard deposits were noted along the victualic pipes and solid trap with a calculated average deposition rate of 1.6 - 2.0 mm/yr. These values are much lower than those calculated for Palinpinon I, with hot brine injection at SSI≅1.15. Inspections at the ML-1RD, ML-2RD branch lines and mainlines in Palinpinon I showed deposition rates in the order of 1.6 -2.6 mm/yr. However, isolation valves and side valve assemblies showed higher deposition rates ranging from 3.3 - 7.3 mm/yr from molecular sllica deposition. All scales in the hot injection lines are vitreous. hard and compact in nature.

The cold injection at SG-IRD shows minimal deposition along the reinjection line. The low deposition rate was attributed to the high fluid velocity along the reinjection line and the stable nature of the colloidal silica formed. Cooler fluids entering SG-1RD was characterized by $SSI_{cx} \leq 1.0$ and $mSiO_2/tSiO_2 < 0.5$ throughout the duration of the injection. Although, mixing of hot and cold brine was done during some periods of the cold injection scheme, the deposit formed was *soft* and less adhesive and could have been carried by the brine into the fractured formation, thus having negligible effect on the injection capacity of the well.

2.3 BOTONGEDS

The Botong fluids have high silica contents in the brine and high concentrations of the non condensable *gases* (CO_2, H_2S) in the discharge. having tapped the high temperature region of the Bacman reservoir. In this *case,* at typical production separator pressures of 0.70 MPaa, the Botong wells will have a combined SSI = 1.40 and NCG levels of 6%. Increasing the separator pressure to levels close to amorphous silica saturation, decreases the power output and increases the NCG levels to unacceptable values. Furthermore, reservoir modeling has indicated the possibility of pressure drawdown in this sector of the field, and could consequently result in reservoir boiling producing concentrated silica-rich brine.

OP-4D and OP-3D are the major contributors to the brine flow at Botong. Based on the success of the medium term discharge testing of OP-4D using a cold injection scheme the Botong Effluent Disposal System (EDS) was conceptualized (Solis et al., 1995). In *this* scheme (Fig. 4), two-phase fluids from the wells is initially flashed at the production separator at 0.70 MPaa, followed by a second flash at atmospheric pressure. The fluid flows into a baffled thermal pond, for sufficient cooling and deposition of silica. The silica reduced brine, then flows into a deaentor pond where steam from the second flash is used to heat the brine to expel dissolved oxygen, thus preventing corrosion along the pipelines. The silica reduced brine is then flowed by gravity through victualic pipes and injected into OP-2RD.

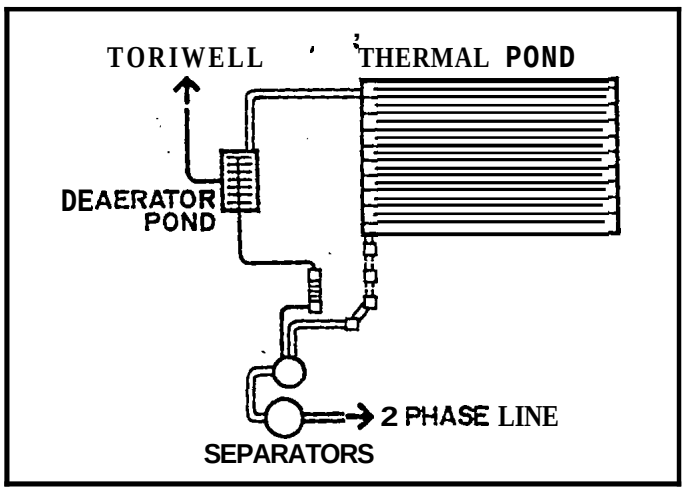


Fig. 4. The Botong Effluent Disposal System.

This scheme was tested in March, 1995 to establish the operating conchtions of the EDS. Other objectives included improving the quality of silica deposited in the pond, and to look into other methods of waste brine disposal. Brine collected after the first flash separator was highly saturated in silica with SSI values rangng from 1.5-1.6 confirming predictions. Hard compact, vitreous deposits formed at the first flash vessel and the lines before the second flash vessel suggest deposition rates of >3 inches/yr. which translate to about 82% of a 10 inch pipe blocked in one year of operation.

The thermal pond was successful in depositing some silica with an efficiency of about 51% at water flows close to 25 kg/s, and a residence time of about 6 hours. The SSI_{Ce} at the final sampling point (FSP) is at 1.3, while SSI_{Cx} based on monomeric silica is <1.0. At maximum settling and deposition of silica in the pond, total silica production was calculated at 1.7 tons/day, while wet slurry production is estimated at 36 tons/day. However, the small fluffy, gelatinous. non-cohesive precipitate formed is readily carried by the flowing water and does not immediately settle by gravity. Throughout the duration of the testing, gelatinous precipitate was carried by the flowing brine. At the deaerator pond, dissolved oxygen was expelled but the heat redissolved the silica, increasing the monomeric silica in solution although not sufficient to breach the amorphous silica solubility

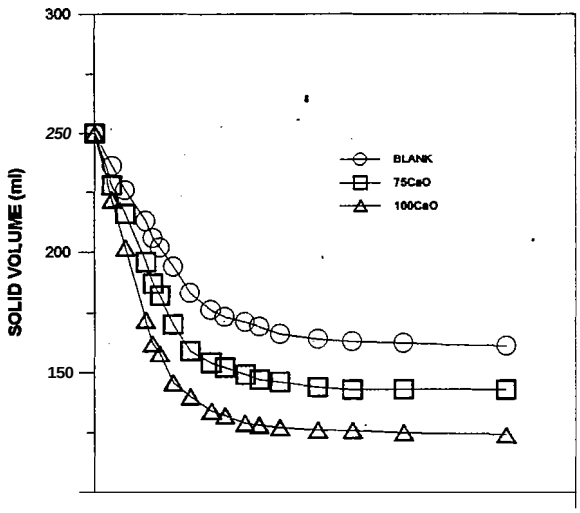
Table 4. Representative Botong EDS chemistry with OP-3D and OP-4D on line to the FCDS.

Source	pH	t°C	mSiO2	tSiO2	DO	SSICe	SSICx	mSiO2 / tSiO2
TPinlet	7.32	93.0	459	1382	1.5	4.1	1.0	0.3
TPoutlet	7.57	35.7	203	794	5.6	5.6	0.9	0.3
DP	7.14	72.2	233	657	3.2	2.6	0.6	0.4
FSP	7.70	68.3	244	492	3.0	2.0	0.7	0.5

The trials were conducted for two weeks. but were abruptly concluded due to decrease in thermal pond efficiency. Silica deposition in almost all the lanes caused the blocking of several lanes. Fluids entering the thermal pond were by-passing half of the lanes and exiting directly to the outlet. In this manner, there was insufficient residence time for the brine to cool and to deposit silica, eventually brine entering the well was silica rich. Maximum silica deposition was achieved in the middle lanes (6,7,8) and progressively decreases down to Lane 20.

It was recognized, that deposited slurry in the thermal pond should be disposed of regularly. for the thermal pond to be effective. One option considered was to pump the slurry into a dewatering sytem for mechanical separation of the solid fiom the water. Several dewatering equipment were tested in the laboratory. These included a decanter centrifuge, spray dryer, filter press, and an experimental prototype solid-liquid separator. Most of the equipment were not successful in totally separating the slurry into its clear liquid and dry solid components. The solid residue still contained ≥ 40% water. Also. the liquid supernatant or elluent still contained some suspended silica colloids. This is due to the ultrafine nature of the silica particles formed in the thermal pond. TEM measurements gave a size of ~0.38μm for the aggregate and an estimated 30 nm for the individual colloids.

In an attempt to increase the particle size for better settling and separation of the formed silica particles, laboratory scale experiments on flocculation were undertaken. Brine from the thermal pond was treated with known concentration of Ca+2 solution. The results are shown in Fig. 5. Fast settling was observed in the 100 ppm CaO treated slurry. After 20 minutes of standing, the gel volume was reduced to 22%, and 23% after 120 minutes. This indicate that agglomeration of silica with Ca works fast after the thorough mixing and standing of the slurry.



As most of the dewatering equipment available in the market cannot completely separate the slurry into its component dry solid, and clear liquid without any additional processes like heating, other options for slurry disposal were considered. Also, dewatering produces the additional problem of what to do with the solid residue. Until now, no commercial application has been identified, and the only alternative was to dump it at the existing cement lined sump at Pad Y. On the other hand, slurry injection would effectively dispose of all the formed slurry underground To test this, the Botong thermal pond was operated without any restraining baffles at the end of the lanes to retard the flow of formed silica solids. Wooden barriers were erected between lanes to restrict the flow in a circuitous manner to achieve longer residence time, sufficient for the polymerization process to progress to completion. In this manner, formed gelatinous silica solids are maintained as ultra fine particles. The slurry was injected into OP-1RD, a deep well with initial injection capacity of about 46 kg/s. The results of the injection flow measurements and well-head pressure monitoring are shown in Fig. 6.

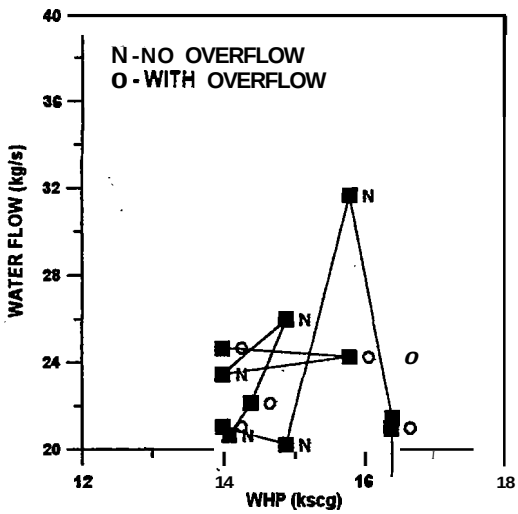


Fig. 6. Relationship of OP-1RD WHP and water flow during the Botong slurry injection trials. Points marked with N-show no overflow in the deaerator pond, while points marked with O- show overflow at the deaerator pond Overflows denote non-acceptance of OP-1RD at the given water flow rate.

The graph shows that initially OP-1RD was accepting fluids even at high injection flows. but after almost a week of continuous slurry injection, there was a serious decline in injection capacity, and increased WHP. The gelatinous precipitate flowing with the brine must have lodged at the pores in the formation causing serious injection loss of the well. This was not observed during OP-2RD injection perhaps because the fracture permeability in this well is greater.

Because of the operational difficulties envisioned in clearing the gelatinous silica slurry being formed in the pond and disposal either by mechanical separation of liquid and solid or by direct injection into a sacrificial shallow well, other options of brine disposal were considered. Hot injection of brine with chemical treatment (acid or chemical inhibitors) were studied because if proven successful, such a system is much easier to manage than a thermal pond Laboratory scale acid treatment trials were undertaken to test the viability of this option, using a silica polymerization vessel developed at IGNS (Brown, 1995). With the polymerization vessel, it is possible to maintain the temperature of the brine at line conditions. and follow the progress of polymerization by taking samples of monomeric silica at regular time intervals. Results of the acid treatment trials are shown in Fig. 7.

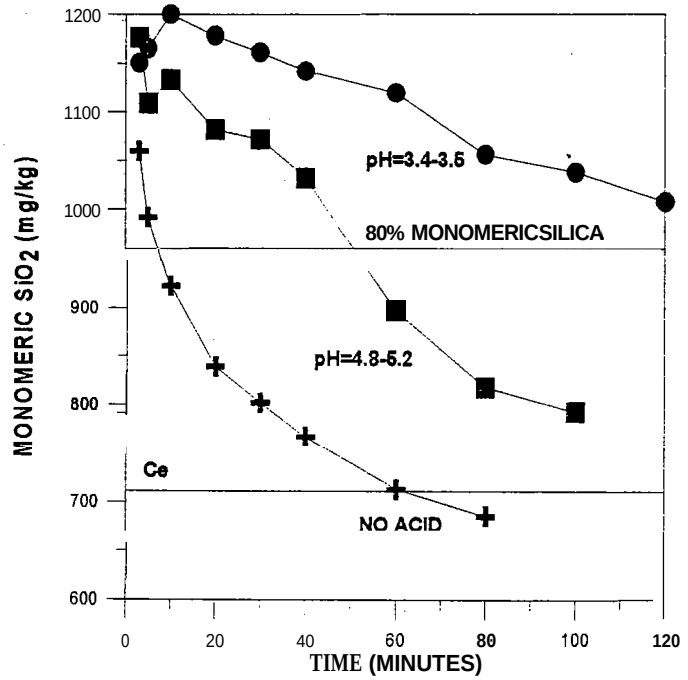


Fig. 7. Acid treatment trials at Botong using the polymerization vessel.

The results confirmed the rapid polymerization of the untreated Botong brine. Retardation of polymerization is achieved only at very low pH (3.4-3.5) where corrosion risks are greater. There is significant polymerization in the pH region of interest (4.5-5.0) within one hour. There is no real induction period or lag time at which polymerization is retarded or stopped even at very low pH. These results suggest that for the Botong brine which has an initial high silica content (–1200 mg/kg), acidification cannot prevent silica deposition during hot injection.

The only remaining option for hot injection of the Botong brine is if treatment with a chemical inhibitor is successful. This is based on the promising results obtained using an experimental inhibitor (DP3439) at SSI ≅ 2.0 and close to 100°C line temperatures. The possible inhibitive action of this compound is to prevent the polymerized silica to reach a critical size, and additional disperse them in

solution such that they do not deposit into pipe walls. Pilot scale testing of this inhibitor are underway, as its action may be brine and temperature specific.

It was earlier recognized that loss in injection capacity may be related to the behavior of the silica gel in the accepting formation. To address this concern formation tests will also be conducted using various test materials ranging from sedimentary, volcanic and regularly shaped synthetic crystals to test the mechanism of deposition in the formation..

3.0 BACMAN I - ACID TREATMENT

As early as 1990, the installation of a binary power plant was being studied to harness the residual heat from the Bacman I waste brine. The combined waste brine of Bacman I has a pH range of 6.5-7.5 and silica concentrations ranging from 700-750 mg/kg. These silica levels translate to an SSI of 0.9-1.0 at the line temperature of 180°C. However if this brine is passed through an Ormat heat exchanger and exits at temperatures of 120°C-125°C, the final SSI will be about 1.50-1.60. At this high SSI, there is a greater risk of silica deposition along the surface pipelines and the well bore.

However, theoretical studies by Makrides et al., (1983) have shown that silica concentrations ranging from 740-800 mg/kg remain stable in solution at temperatures of 95°C for 3 hours if the pH is maintained at 5.5. Since polymerization is catalyzed by OH, the addition of the acid causes the reaction to be very slow, thus the deposition rate is also very low. The addition of the acid to a supersaturated silica solution prevents the reaction of ionized and unionized silicic acid, thus preventing polymerization for short periods of time. However it should be emphasized that this is just a kinetic effect. Polymerization can be effectively halted for limited periods of time but not completely stopped. This delay in polymerization should be sufficient for the brine to go through the reinjection lines, the well bore, and preferably long distances from the well bore.

Acid treatment was considered an attractive silica mitigation scheme for the Bacman I brine due to the moderate amounts of silica (700-750 mg/kg), where this scheme is known to have worked (Brown, 1995, Brown and McDowell, 1983). Since each brine is unique, and the amount of acid needed to change the pH where polymerization is delayed depends on the presence of several buffers in solution, actual experiments on the Bacman I brine were undertaken. This experiment is required to find the optimum pH where the induction period is stable for long periods sufficient for the brine to reach the formation and away from the well bore.

Calculations using the likely flow rates of the reinjection system have shown that there is a theoretical residence time of about 30 minutes from the point of injection to the bottom of the reinjection well (Pal-1RD or Pal-4RD). Any acid modification scheme must have an induction period that should not be less than 30 minutes to ensure that the brine has reached the formation before any deposition begins. The premise here is that the huge volume of the reservoir can cope with silica deposition, while the limited area of the brine lines and the well bore cannot. In addition, the high temperatures in the reservoir would increase the solubility of silica such that it does not precipitate close to the well.

3.1 TITRATION CURVE

Titration curves were established using the combined brine from the Bacman I power plant (Fig 8). The brine is collected using a cooling coil from the brine line into a tightly capped sampling bottle to prevent gas lost. The sample is cooled and titrated with 0.01N H_2SO_4 at 25°C. From the titration curve it was shown that 3.5-3.8 ml of 0.01N H_2SO_4 is required to bring the pH of 100 ml of Bacman I brine to pH–5.5. Initial calculations also suggest that acidification of the 350 kg/s of Bacman I brine will incur an annual cost of about 2 million pesos.

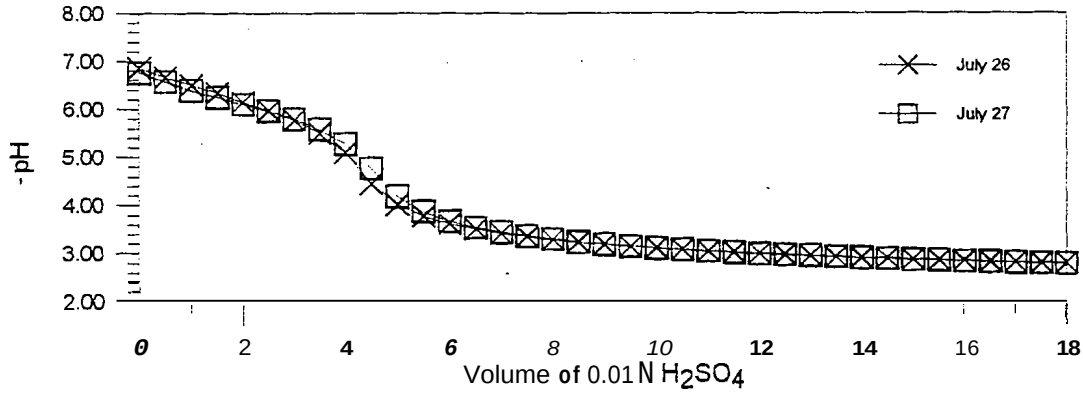


Fig. 8. Bacman I titration curve conducted at 25°C using 0.01N H_2SO_4.

3.2 POLYMERIZATION CURVES

The polymerization experiments were carried out using a polymerization apparatus developed by IGNS in New Zealand (Brown. 1995). A polymerization curve is prepared at 120-125°C (the theoretical outlet temperature of the binary heat exchanger) to serve as control in assessing the applicability of the pH modification scheme. Polymerization curves were also prepared at pH =5.0 and 5.5. The calculated acid volume is introduced to the sampling loop at line temperatures (176-180°C). The hot brine is then introduced with the acid into the polymerization vessel. As soon as the acid is properly *mixed* in the chamber. the brine flowing through the cooling coil will be abruptly cooled with cold water to reach the binary outlet temperature of 120-125°C. The temperature of this, brine is monitored by a thermocouple. The cooled 120-125°C brine is used to maintain the temperature in the polymerization vessel. Samples for monomeric and total silica are collected at appropriate time intervals for a period of three hours. Samples for pH determination are also collected at the start and end of the experiments and the pH determined at 25°C. The pH modification trial set-up is shown in Fig. 9.

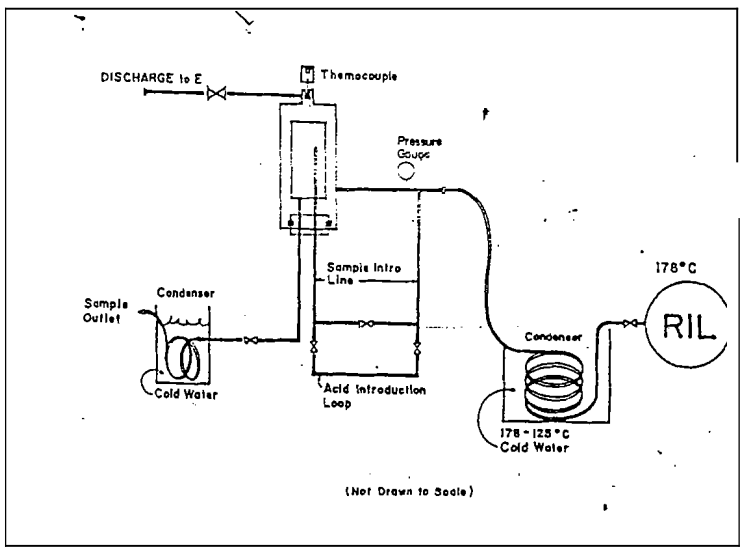


Fig. 9. pH modification trials set-up.

The results of the silica polymerization trials are shown in Fig. 10. A rapid polymerization of untreated brine is observed as temperature is dropped from 176°C - 122°C. The equilibrium amorphous silica solubility (Ce) is reached within 60 minutes. At this point complete polymerization is achieved and deposition of polymerized silica is expected to occur.

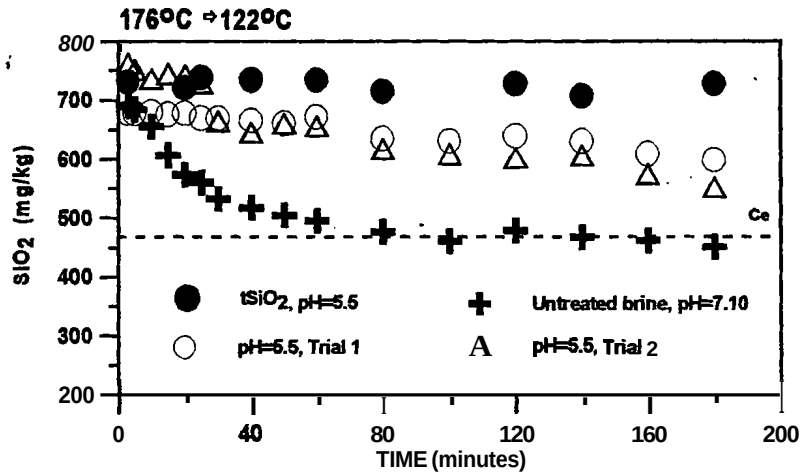


Fig. 10. Polymerization trials of acid treated Bacman I brine at pH =5.5, and temperature dropped from 178°C to 122°C.

However, if the brine is acidified to pH=5.5, there is a corresponding delay in polymerization, with an induction period close to 60 minutes after which the monomeric silica concentration gradually drops denoting the onset of polymerization. Total silica concentrations remain stable for 3 hours, sufficient for the brine to reach the formation without colloidal silica deposition for the Pad RA injectors (Pal-1RD, -4RD). Therefore hot injection (121°C or greater) with acid treatment is the recommended brine disposal scheme for the commercial operation of the Bacman I binary power plant.

4.0 CHEMICAL INHIBITION - MALITBOG

One of the outstanding technical difficulties faced by PNOC-EDC in the operation of its geothermal fields is in obtaining and maintaining adequate line and injection capacities due to the deposition of amorphous silica in surface pipelines and injection wells. One of the thrusts adopted to provide a long term solution to this operational problem is to test the use of chemical additives to inhibit the growth of amorphous silica scales in supersaturated geothermal brines.

PNOC-EDC in cooperation with FMC Process Additives Division has been experimenting with chemical additives using pilot facilities in Malitbog. The inhibition experiments were carried out at well 501 and 5R7D at the Malitbog sector of the Leyte Geothermal Project. The process flow diagram of the test facilities are shown in Fig. 11. Well 501 is discharged into a separator vessel at a fixed WHP, temperature, water flow and silica saturation index. The waste brine is split equally into two parallel lines, one serving as blank (B) while the other is dosed with fixed line concentration of the additive (A). The fluids then converge and are either injected into 5R7D or discharged to the environment at restricted flow rates. The lines are run at these specified conditions for a period of 2 to 4 weeks. At the end of the flowing tests, the deposition spools at all sections of Lines A and B were inspected to document the nature and thickness of the deposits formed Water flow along the lines was measured regularly using $MgCl_2$ as tracer (Seastres, et al., 1994).

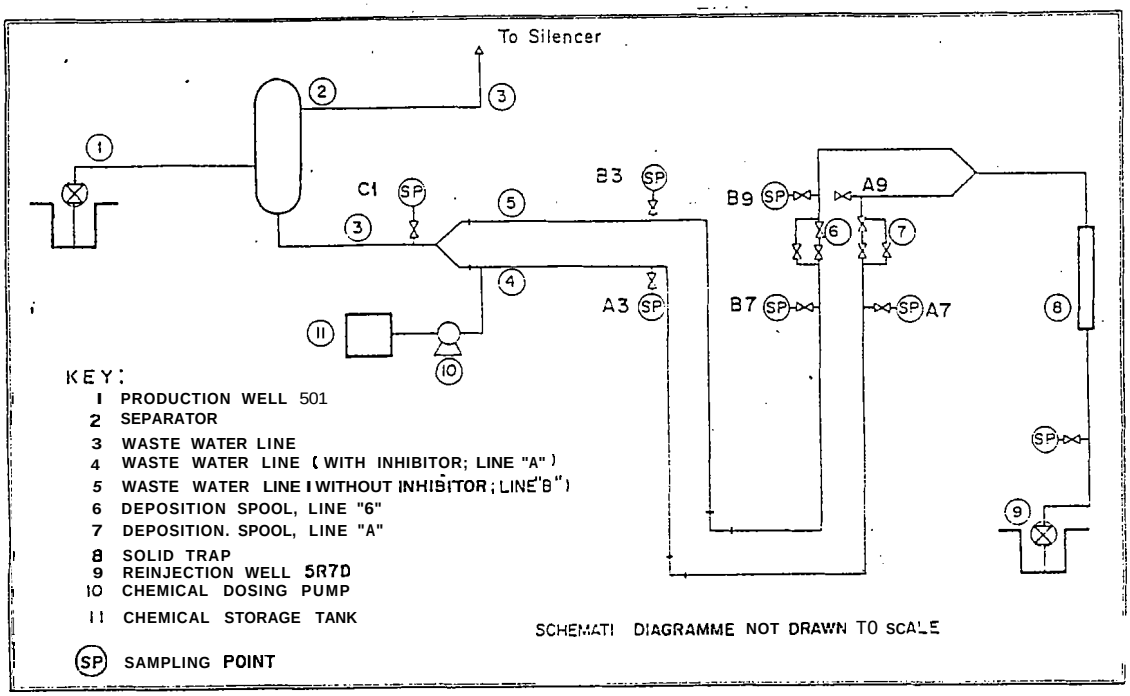


Fig 11. Experimental field design and set-up of the Malitbog pilot facility for testing chemical additives formulated for the inhibition of amorphous silica scaling in brink lines.

Among several tested chemical combinations. an experimental mixture with code name DP3439 has showed a significant reduction of **amorphous** silica deposition in geothermal **brines.:** Results of the trials using 6" insulated pipes with brine at very low **flow** rates of 1.5 **-5.4** kg/s and at extremely high silica saturation index of 2.3 -2.5 at line temperatures of 105°C - 110°C have established that DP3439 has effectively decreased amorphous silica deposition even at low concentrations of **the** additive.

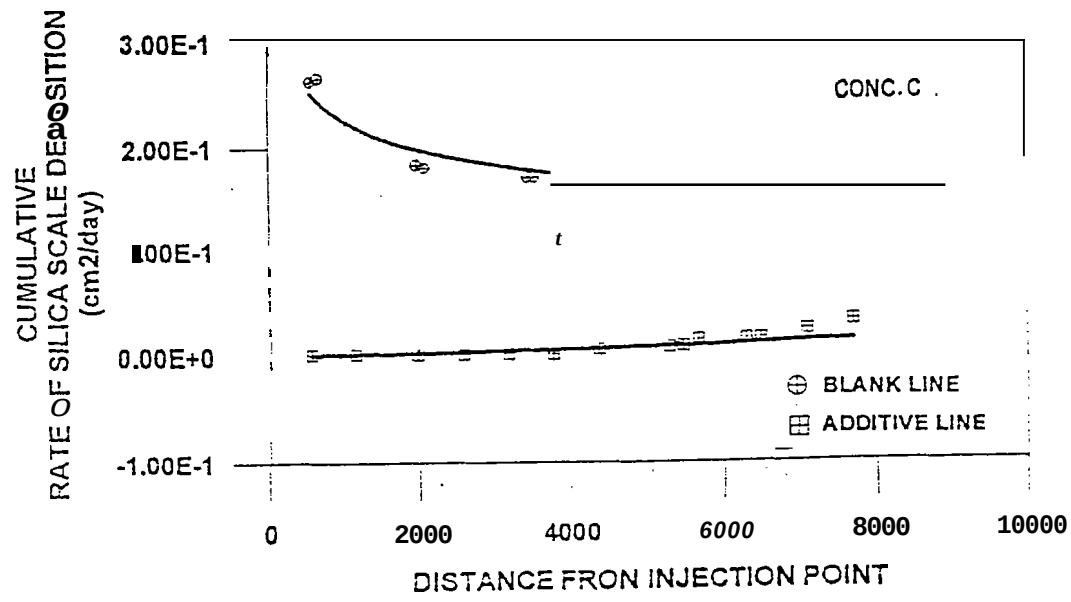


Fig. **12.** Comparison of deposition rates of treated line **(A) and** blank line (B) at concentration (C). showing the effective inhibition of amorphous silica scaling **with** DP3439

The reaction mechanism governing the inhibitive action of DP3439 does not seem to be involved with the prevention or holding of monomeric silica from transition into the polymeric state. Monomeric silica concentrations measured at several points in the line showed that monomeric silica decreased independently of the concentration of the chemical additive. The inhibitive action of DP3439 could be centered on the prevention of polymeric silica into reaching a critical size, such that they remain suspended in solution. Scanning electron microscopy (SEM) results show that particle sizes in the blank line are definitely larger than those obtained from the treated line, for the same area and magnification.

The results of the pilot tests are very promising, because the inhibitor worked at brine fluid conditions more severe than those existing in our present FCDS. If this results *can* be translated into our existing FCDS, there would be enhanced flexibility in adopting lower production separator pressures to increase *steam* recovery or *cascade* the brine into heat exchangers where additional power *can* be generated. Actually, the applications are staggering and *only* the *cost* of the chemical *may* limit its economic viability. The chemical now marketed as "Geogard" is being tested at the Sambaloran lines of the Leyte Geothermal Project for optimization studies of its effectiveness under actual FCDS conditions.

5.0 CONCLUSIONS

All of the cold injection schemes discussed have produced gelatinous, porous, *soft,* low bulk density non adhesive type of deposit, of which a fraction settled in the sumps or ponds, but a majority was carried by the flowing brine into the well and the receiving formation. Retaining the brine in sumps or ponds at lower temperatures is a conscious attempt to convert much of the dissolved silica into the relatively non-adhesive polymeric form, or to reduce dissolved silica concentration by allowing time for its conversion into the colloidal silica form. This goal was attained in all of the cold injection schemes, and the monomeric silica monitored at the outlets of the sumps or ponds have been reduced to concentrations below the amorphous pseudo-equilibrium saturation. The unavailability of the molecular dissolved silica to cement coagulated silica into adherent gel or solid scale prevented the formation of hard *scales* in surface retaining sumps or ponds, pipelines and the well bore. In fact, for NASUJI the colloids formed are *so* stable, they *can* remain suspended in solution for more than six hours. The *success* of the cold injection schemes in MlGP and NASUJI, *can* thus be attributed to the formation of this relatively non-adherent gel, and the high fracture permeability of the receiving formation as manifested by the high injection capacity of the injection wells.

However, slurry injection at Botong resulted in the loss of injection capacity of OP-1RD. This *may* be due to the larger silica particles formed in Botong from the much higher concentration of silica of brine and the long residence time in the pond. The silica floc or gel was carried by the brine in the reinjection well and accumulated where the brine entered pores or cracks in the formation capable of filtering it. These places eventually clogged up. Injection of slurry at Botong will thus merit success, only if we *can* find large fractures such that the gel *may* come to rest as far away from the well bore and not affect its injection acceptance.

Since the formation has a great effect on the stability of the colloid or gel, formation studies are recommended to look into suitable materials that are permeable to the Botong silica gel. This must be actively pursued, to have alternative options if hot injection with chemical inhibition fails.

Laboratory scale studies using a polymerization vessel show the feasibility of acid treatment with H_2SO_4 as a silica mitigating measure for the proposed Bacman I binary power plant which will bring SSI saturation from 1.0 to 1.60 by dropping the temperature of the brine from 180°C to 121°C. At pH=5.5, there is a delay in polymerization of close to 60 minutes, which is sufficient for the brine to reach the formation using the Pad RA injectors (Pal-1RD and Pal-4RD). Therefore hot injection (121°C

or greater) is the recommended brine disposal scheme for the commercial operation of the Bacman I binary power plant.

Pilot scale tests at Malitbog using a chemical additive DP3439 have shown a significant reduction in amorphous silica deposition from geothermal brines. Results of the trials using 6" insulated pipes with brine at very low flow rates of 1.5 -5.4 kg/s and at extremely high SSI of 2.3 - 2.5, line temperatures of 105°C - 110°C have established that DP3439 has effectively decreased amorphous silica deposition even at very low concentrations of the additive: These results are very promising because the inhibitor worked at brine fluid conditions more severe than those existing in our present FCDS. If these results can be translated into our existing FCDS, there would be enhanced flexibility in adopting lower production separators to increase steam recovery or to cascade the brine into heat exchangers where additional power can be generated The chemical now marketed as "Geogard" is being tested at the Sambaloran lines of the Leyte Geothermal Project for optimization studies of its effectiveness under actual FCDS conditions.

ACKNOWLEDGMENTS

The authors would like to thank PNOC - Energy Development Corporation for permission to publish this report. We would also like to acknowledge the numerous individuals from the Geoservices Section who contributed to the actual implementation of these studies in the field.

REFERENCES

Amorsson, S. (1995) Silica in geothermal waters: conditions for its deposition and methods to prevent it. In: Course on Injection Technology. WGC Pre-congress short course, Pisa, Italy, pp. 95 - 109.

Brown, K. (1995) In country training programme: silica geochemistry. Confidential report prepared for PNOC-EDC.

Brown, K. L. and McDowell, G. D. (1983) pH control of silica scaling. Proc. 5th NZ Geothermal Workshop, 157-175.

Chan S. H. (1989) A review on the solubility and polymerization of silica. *Geothermics*, 18, 49-56.

Fleming, B. A (1986) Kinetics of reaction between silicic acid and amorphous silica surfaces in NaCL solutions, *J. Colloid Interface Sci.*, 110, 40-64.

Fournier, R. O. and Rowe, J. J. (1977) The solubility of amorphous silica in water at high temperatures and high pressures. ***Am. Min.*, 62,** 1052-1056.

Garcia, S. E., Jordan, O.T. and Macambac, R V. (1993). Prevention of silica scale formation in geothermal environments using chemical methods. Progress Report No. 1, PNOC-EDC Internal Report (unpublished report).

Garcia, S. E., Jordan, O.T. and Macambac, R. V. (1994). Prevention of silica scale formation in geothermal environments using chemical methods. Progress Report No. 2, PNOC-EDC Internal Report (unpublished report).

Iler, R. K. (1979) The chemistry of sllica. New York: John Wiley and Sons

Makrides, A C., Turner, M. and Slaughter, J. (1980) Condensation of silica from supersaturated silicic acid solutions. *J. Colloid Interface Sci.*, **73**:2, 345-367.

Mrockzek, E. K. and Reeves, R R (1994) The effect of colloidal silica on silica scaling from geothermal fluid Proc. 16th NZ Geothermal Workshop, 97-101.

Seastres, J. S. Jr., Jordan O.T., Barroca, G. B. Reyes, R L., Macambac, R V., Solana, RS., Solis, R P. and Cabel, A C. Jr. (1994) Assessment of on-line water flow measurements using magnesium chloride as a tracer. PNOC-EDC Internal Report. (unpublished)

Solis, R P., See, F. S., Ruaya, J. R and Cabel, A C. Jr. (1995) Low temperature waste water injection experiments at the Bac-Man geothermal field, Philippines. Proc. of the World geothermal Congress, 1995 Vol. 3,2005-2010.

Weres, O., Yee, A. and Tsao, L. (1981). Kinetics of silica polymerization. *J. Colloid Interface Sci. 84,* 379.