

ANALYSIS OF BLOCKAGES FORMED DURING INJECTION OF A POLYACRYLATE BASED CALCITE ANTI-SCALANT CHEMICAL

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ABSTRACT

Four cases of blockages and deposition of injection tubings used for calcite inhibition systems are presented. Blockages inside injection tubings were caused by: 1) dehydration and crystallization upon flashing of inhibitor, 2) thermal degradation of inhibitor resulting in insoluble products, 3) corrosion products from surface facilities, 4) incomplete filtration of impurities in water used for dilution of chemical. FT-IR spectra shows the thermal degradation of the polyacrylate at $T \geq 240^\circ\text{C}$. Likely product is a polyanhydride, which is expected to have a rigid backbone and lesser solubility in water. The polyacrylates also precipitate through cross linking forming a gel network in the of S or S containing compounds at high temperatures. The black tar like material formed is insoluble even to the most aggressive cleaning agent. At higher temperatures ($>280^\circ\text{C}$), thermal degradation results in complete breakdown of the polymer back bone and lost of inhibition. There is also evidence of high temperature corrosion inside the capillary tubing in the presence of S. Petrographic and thermodynamic calculations have shown the presence of stable NiS products at 280°C . Use of polyacrylate based anti-scalant chemical formulations should be limited to geothermal wells where injection temperature is $<250^\circ\text{C}$. Recommendations to avoid similar blockages in injection tubings used for calcite inhibition systems are forwarded.

1.0 INTRODUCTION

Calcite deposition in some geothermal wells of PNOC-EDC has been arrested by the use of Nalco 9354, an acrylate polymer chemical. In 1999, a calcite inhibition system (CIS) was installed in well SP-4D, using a 1/4" capillary tubing for injection. By year 2000, APO-1D was put on commercial operation with a similar calcite inhibition system. In both SP-4D and

APO-1D, blockage of the injection system was encountered during their early operations.

Another calcite inhibition system was installed in well MO-2 in October 2000. The injection of Nalco 9354 was successful in preventing deposition of calcite in the wellbore. However, during tubing pull-out it was observed that several meters of the outer part of the tubing had adherent black deposits.

In 2001, calcite inhibition systems were similarly installed in wells MG-1 and MG-19 with Nalco 9354 as anti-scalant chemical. In well MG-1, the system has been in operation for about 6 months without any injection problems, but with initial evidence of apparent inhibition failure. However, in well MG-19 after only 5 days of operation the tubing was blocked at the bottom end resulting in high pressures and no flow conditions.

Plugging of injection tubing is a common problem (Benoit, 1990, Moya and Yock, 2001) in calcite inhibition systems all over the world. Nalco 1340, another acrylate polymer has a record of tubing blockages at Dixie Valley and the Miravalles field in Costa Rica (Benoit, 1990; Moya and Yock, 2001). The hard deposit formed is insoluble to most cleaning agents. It is believed that plugging is caused by the presence of S, a catalyst in the production of Nalco 1340.

This paper presents a comprehensive chemical analysis of the blockages and deposits in the injection systems of PNOC-EDC wells. It also attempts to establish the genesis or cause of the blockages and recommend preventive methods in future applications.

2.0 CASE HISTORIES OF DEPOSITS AND BLOCKAGES

2.1 In Well APO-1D

Two separate incidents of tubing blockage were reported for wells APO-1D and SP-4D, MGPF in the year 2000. Both wells were utilizing a 1/4" capillary tubing fitted with a nozzle at the tip and weighed down with sinker bars of around 70 kgs each for injection. Both wells tap into 240°C reservoir fluids for production.

After a month of stable downhole injection in APO-1D, it was decided to make the CIS permanent. This involved the transfer of the tubing spool from the truck to a permanent base near the wellhead. During transfer of the spool to the cement base, the inhibitor injection was stopped for a period of about 30 minutes to 1 hour. When the injection was resumed, high-pressures of 900 psig and higher was encountered, from the original stable 200 psig. At this high pressure, only 8LPH were being injected from the original requirement of 16LPH. It is believed that in the short period where no pumping was occurring, the inhibitor solution in the tubing flowed and flashed due to the absence of high-pressure replenishment.

Due to this abnormal condition, the tubing was pulled out on the same day to check for blockage, which is suspected to be causing the pressurization of the line. Indeed upon tubing pull-out, a 2-inch portion of the bottom end was blocked with a black adherent deposit which cannot be dislodged by simple water injection (Fig. 1). A 1-meter portion of the tubing from the tip was cut to remove all blockages. The tubing was washed with water to check if all blockages were cut-off and then re-installed inside the well. The injection system has now been in operation (from June 2000 to present) in APO-1D, without any further incidence of blockage. The cut portion of the tubing with the blockage was sent to Nalco for chemical analysis.

The results of the chemical analysis are shown in Table 1. Analysis of the 105°C dried sample suggest that major component is 57% S (as SO₃), 22% Ni (as NiO), 6% Fe (as Fe₂O₃) and 1% Cu (as CuO). The loss at 925°C, which includes all organics (carbon, hydrogen, nitrogen) or CH₂Cl₂ extractables, many sulfur compounds, water of hydration and CO₂ from most carbonates was about 28%. Nalco

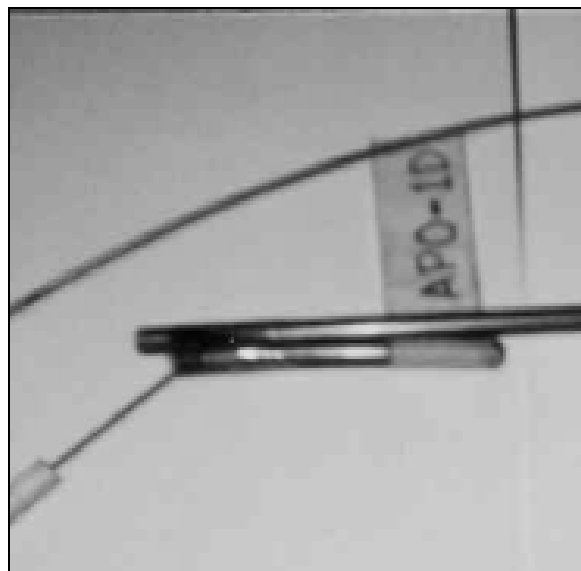


Figure 1. Blocked APO-1D capillary tubing nozzle tip. The pointer shows the 2 inch blockage at the tubing end. The rest of the 1400 meter tubing is free from blockage.

Table 1. Nalco Analysis of APO-1D capillary tubing deposit (1000 m Downhole).

Analysis of 105°C Dried Sample (Weight Percent as Oxide)	
Sulfur as (SO ₃)	57
Nickel as (NiO)	32
Iron as (Fe ₂ O ₃)	6
Copper as (CuO)	1
Carbon (%)	1.2
Hydrogen (%)	0.6
Nitrogen (%)	<0.3
Carbonate (%CO ₂)	<1
Loss at 925°C (%)*	28
*The loss at 925°C includes all organics (C, H, N) CH ₂ Cl ₂ extractables, many sulfur compounds, water of hydration and the CO ₂ from most carbonates.	
The following elements were not detected (<1%): Na, Mg, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Co, Zn, Sr, Sn, Ba, Pb	

Lab Comments:

Infrared Spectroscopy Results: Infrared spectral analysis of dried sample indicated the presence of inorganic species (primarily sulfates) and hydrated inorganics. There was no evidence of organic material in the deposit. In particular, there was no evidence of polyacrylate in the deposit.

The loss on ignition is approximate due to limited sample. There was insufficient sample to run a CH₂Cl₂ extraction.

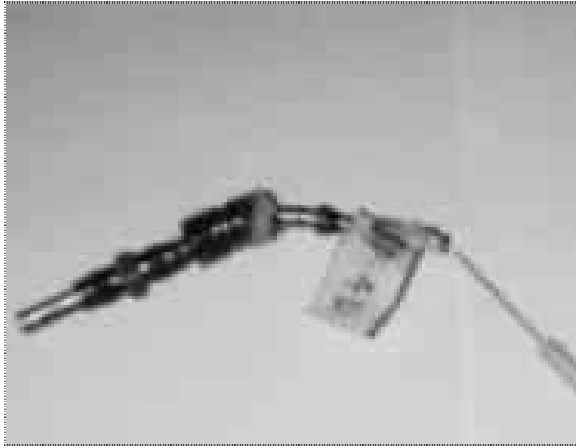


Figure 2. Blocked SP-4D capillary tubing nozzle tip. The pointer shows the 1 inch blockage .

performed infrared spectral analysis of the sample but detected no clear polyacrylate signature, instead reported the presence of inorganic species specifically sulfates. Attempts to re-dissolve the deposit with various organic and inorganic cleaning agents (e.g. 48%HF at 70°C, 10 g NaOH with 100mL ethanol below 50°C, CHCl_3) failed.

Petrographic analysis of the same sample identified ~70% amorphous and non-metallic material likely the dried inhibitor chemical. About 30% nickel sulfide (Ni_3S_2 -

heazlewoodite?) occurring as coarse subhedral grains attached to the capillary tubing and also as fine to very fine grained anhedral masses scattered on the surface of the amorphous organic material were identified. Trace amounts ($\ll 1\%$) of magnetite (Fe_2O_3) exists as very fine slender grains (J. B. Rossel and M. C. Zaid-Delfin, 2001). Trace amounts of magnetite suggest low temperature corrosion of non-stainless steel portions (galvanized) of the surface feed system (e.g. gate valves, joints, pressure probes). The surface injection facilities should have been completely made up of stainless steel and PVC but some gate valves, pressure probes and check valves had to be replaced prior to commissioning due to low pressure rating. FT-IR spectra of the dried deposit is identical to the original neat Nalco 9354 (Fig. 2) spectra showing absence of thermal degradation.

2.2 In Well SP-4D

In December 2000, the injection system of SP-4D was pulled out after only a week of installation due to a suspected blockage at the injection head as monitored from high injection pressures and cessation of flow. The blockage occupied a 2-inch portion of the injection tip (Fig. 3). The blockage incident was preceded by a short period of brownout. The brownout occurred on a weekend, and the pull-out of the

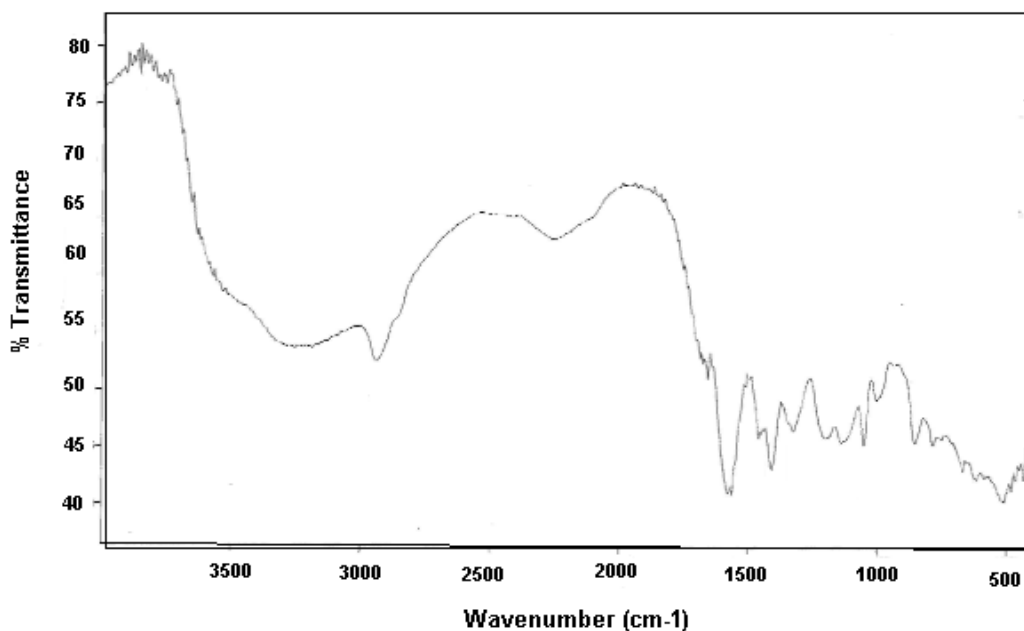


Figure 3. The original FT-IR spectra of neat Nalco 9354 coincides with APO-1D deposit showing absence of thermal degradation.

tubing could only be done after more than 2 days of high-pressure conditions. Curiously, no blockage incident was reported for well APO-1D, which was in the same pad with similar injection set-up as SP-4D. The only difference between the two injection set-ups was the chemical dosing pump models. For APO-1D, the dosing pump is a Neptune model 525, while SP-4D has a Neptune model 532.

Chemical analysis of the deposit as performed by NALCO is shown in Table 2. Analysis of the 105°C dried sample suggest that major component is 47% S (as SO₃), 46% Ni (as NiO), 3% Fe (as Fe₂O₃) and 1% Cu (as CuO). The loss at 925°C which includes all organics (carbon, hydrogen, nitrogen) or CH₂Cl₂ extractables, many sulfur compounds, water of hydration and CO₂ from most carbonates was about 21%. Nalco performed infrared spectral analysis of the sample but detected no clear polyacrylate signature, and instead reported the presence of inorganic species specifically sulfates.

Since no FT-IR spectra was provided to PNO – EDC, an independent analysis was performed on the same sample from SP-4D at the UP Analytical Services Laboratory. The FT-IR spectra is shown in Figure 4. The FT-IR spectra still show the definitive –OH stretch distinct to –COOH groups, C-O stretch close to 1100, and strong bands at 400-800 likely from =CH₂ deformation modes.

The findings from three independent laboratories would suggest that the deposit is composed of dried chemically altered inhibitor (from FT-IR, elemental and microscopic studies) in amorphous form and high temperature metallic corrosion products (nickel sulfide). Low temperature corrosion of non-stainless portions of the surface injection facilities persists as shown by the presence of Fe₂O₃. Although, Nalco claims that there is no evidence of the polyacrylate in the FT-IR spectra, the spectra clearly indicates organic bands that could only come from the thermally degraded polymer from long term (more than 2 days) exposure to high temperature. The FT-IR spectra even suggest presence of =CH₂, which is a by-product of chain scission (See reactions below) under, heated conditions. Also, elemental analysis showed the presence of S, which is an impurity in the formulation, used in the synthesis of the polyacrylate. These alterations in polymer

Table 2. Nalco Analysis of SP-4D capillary tubing deposit (1000 m Downhole).

Analysis of 105°C Dried Sample (Weight Percent as Oxide)	
Sulfur as (SO ₃)	47
Nickel as (NiO)	46
Iron as (Fe ₂ O ₃)	3
Copper as (CuO)	1
Carbon (%)	<0.3
Hydrogen (%)	0.5
Nitrogen (%)	<0.3
Carbonate (%CO ₂)	<1
Loss at 925°C (%)*	21
*The loss at 925°C includes all organics (C, H, N) CH ₂ Cl ₂ extractables, many sulfur compounds, water of hydration and the CO ₂ from most carbonates.	
The following elements were not detected (<1%): Na, Mg, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Co, Zn, Sr, Sn, Ba, Pb	
Lab Comments: Infrared Spectroscopy Results: Infrared spectral analysis of dried sample indicated the presence of inorganic species (primarily sulfates) and hydrated inorganics. There was no evidence of organic material in the deposit. In particular, there was no evidence of polyacrylate in the deposit.	
The loss on ignition is approximate due to limited sample. There was insufficient sample to run a CH ₂ Cl ₂ extraction.	

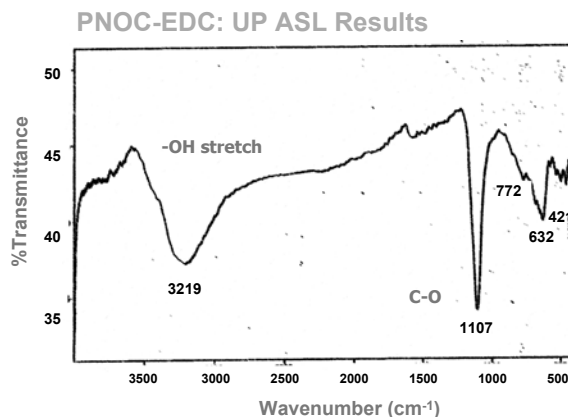
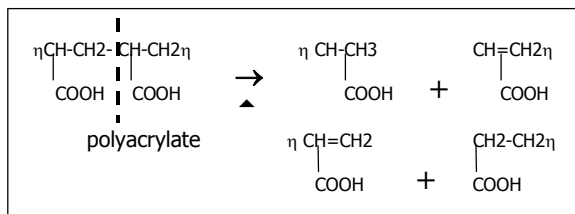


Figure 4. FT-IR spectra of SP-4D deposit at end of tubing with advanced thermal degradation of polymer backbone.

structure produced an adherent less soluble polymer. Another problem associated with Nalco 9354 is the presence of S and its reaction with the Ni alloy of the stainless steel tubing to produce high temperature corrosion products, like nickel sulfides.

Thermal degradation of the polyacrylate can result in bond cleavage at various portions of the polymer (random chain scissions). The degradation can result in a mixture of products from the following reaction depending on the temperature of exposure:



Thermal degradation can form products with unsaturated bonds (C=C) resulting in colored residues. It should also be noted that if bond breaking occurs at the backbone, and no bond breaking occurs at the -COOH functional group, the major absorption frequencies remain, with addition of peaks for -CH₃ and =CH₂ groups formed. Since the FT-IR spectra (Fig. 4) has been altered from the original spectra (Fig. 2), it is believed that thermal degradation through chain scission has occurred. Thermal degradation has progressed to a point detrimental to inhibition or lost of inhibiting properties of the polymer.

2.3 In Well MO-2

Well MO-2 was put on calcite inhibition last September 30, 2000 using Nalco 9354 as inhibitor chemical. The CIS injection depth was set at 450 mVD at temperatures of 200°C. The chemical injection at 16LPH to make a dosage of 5 ppm in TMF was successful in preventing calcite deposition in the well bore. Last March 31, 2001, the capillary tubing was pulled out to make way for maintenance of the power plant. During pull-out, the crew observed that the tubing was coated cohesively with black deposits, which flaked off upon passing through the pack-off cap. The total length of the tubing with black coating was from 18 mVD to 275 mVD (B. C. Buñing, pers. com.). The coating on the tubing is about 1.0 mm thick. Between 275 mVD to 450 mVD the tubing is generally clean (B. C. Buñing, pers. com.). This is the very first report of deposition on the outside of the capillary tubing used for calcite inhibition systems.

The black deposit, which flaked off from the tubing, was sent to Manila for chemical analysis.

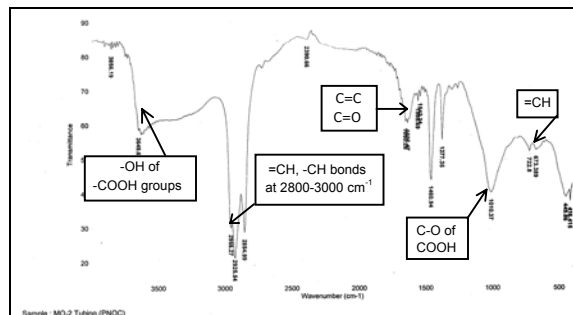


Figure 5. FT-IR of MO-2 tubing deposit showing the additional multiple peaks at the 2900 cm⁻¹ region.

Petrographic analysis of the black sample suggests the absence of corrosion products (S. G. Ramos, pers. com.). FT-IR spectra of the black deposit show the presence of an altered inhibitor (Fig. 5). Major difference in spectra with the original Nalco 9354 is in the 2000 - 3000 cm⁻¹ region or the band for the -CH groups. The original spectra of Nalco 9354 shows a single sharp peak near 2200 cm⁻¹ and a shoulder at 2900 cm⁻¹ overlapping the broad -OH peak from 3000 - 3500 cm⁻¹. However, the black deposit shows multiple bands at 2800-2900 cm⁻¹ suggestive of the presence of -CH₃ and =CH₂ groups instead of the original -CH groups alone. This transition can be attributed to cleavage of the long chain polyacrylate molecule to form smaller polymeric chains (See above chain reactions).

Initially, it was thought that deposition occurred due to overdosing in the initial stages of inhibition. Review of the dosing records show actual variable dosage concentrations ranging from 4 to 8 ppm in total mass flow (Fig. 6). The dosage is variable due to disparity between calculated and the actual prepared solution. Such a large variation in solution preparation cannot be tolerated. After a month of preparation, the precision of the actual injectate solution should be within acceptable limits of ±10-15% difference, considering bulk preparations. However, the Manito data shows a large variable range (-100 to 80% difference), which is unacceptable even for bulk preparations in a period of 6 months (Fig. 6). There is a need to review preparation methods and measuring equipment to ensure standard acceptable limits for solution preparation. The limitations of preparation at Manito are due to the crude interconnected drums; transfer pumps which limit solution mixing. The feed system is

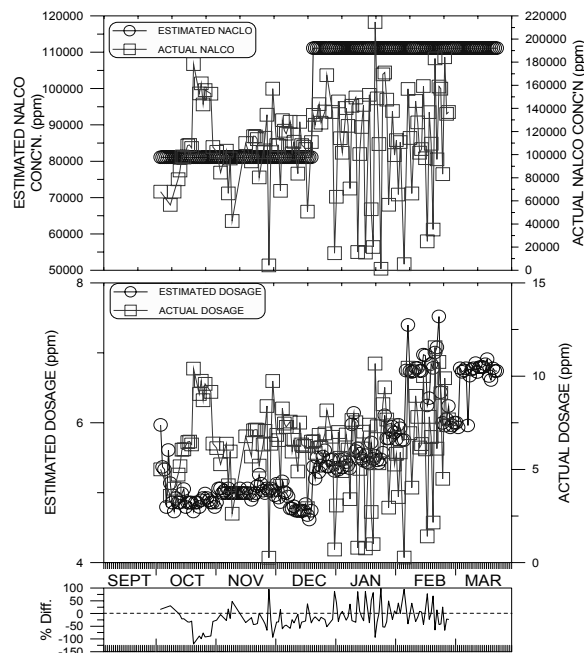


Figure 6. Monitoring of dosage parameters during the 6-months MO-2 calcite inhibition trials.

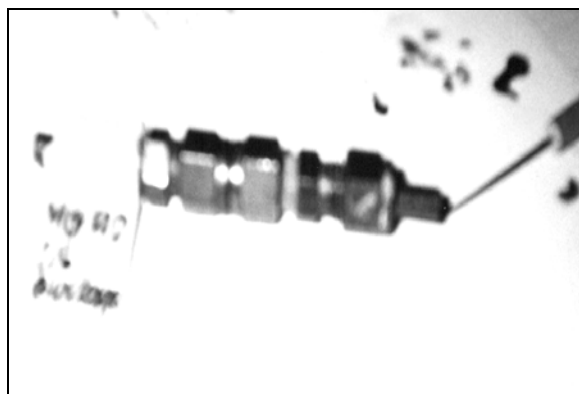


Figure 7. Blocked MG-19 capillary tubing nozzle tip. Only a ~5 mm portion of tip has a very hard deposition which completely blocked the tubing.

Table 3. Nalco Analysis of MG-19 capillary tubing deposit

Insufficient sample was available for standard deposit analysis. X-ray analysis was estimated for the inorganic content using an energy dispersive system equipped on a scanning electron microscope.	
The following elemental values have been normalized to 100% as oxides. The major elements have been rounded to the nearest 5%. Minor elements are present at <10%.	
Major	Fe (65%) and S (10%)
Minor	Ni
Trace	Si, Cu, Cr, Cl, P, Ca and Al

not efficient and results in inaccurate dosage concentrations on-line. This problem was not encountered at MGPF and Mahanagdong, which started with a 200-liter measuring tank and a 2,000-liter graduated mixing tank, where re-circulation can effectively mix a bulk solution.

Nalco claims that the FT-IR signature is by an oil and Si (Menchavez, 2001 e-mail communications). Oil based lubricants are usually used during storage of the capillary tubing to protect it from moisture and pitting corrosion. The FT-IR signature of the lubricant is not available for comparison. However, the lubricant was coated on the whole length of the tubing, while the deposition formed only at discrete lengths above the injection point. In the absence of other data, the deposit on the outer portion of the tubing remains unresolved at this time.

2.4 In Well MG-19

Well MG-19 was put on-line with a CIS last September 8, 2001. The injection depth was at 1850 mMD with an injection temperature of ~283°C. After only 5 days of operation, the injection pressure increased from 460 psig to the maximum pump capacity of 600 psig, with decline in dosing flow rate from 15LPH to 1LPH. Zero flows were observed at 40% stroke setting of pump. The stroke setting was changed to 100%, and then fresh water injection was attempted to change the contents of the tubing with water prior to pull-out (Siega, pers com.). The pumps were operational under atmospheric conditions (i.e. when not connected to tubing), but once connection to tubing is resumed maximum pressure is again encountered indicative of blocked tubing. The tubing was pulled out after two days on September 15, 2001. Inspection of the tubing showed a ~5 mm obstruction close to the nozzle tip (Fig. 7). The obstruction is very hard with black adherent deposition. The blockage completely sealed the tubing end removing any possibility of injection once it is formed. The cut tubing with blockage was sent to Manila for chemical analysis.

Nalco performed scanning electron microscope (SEM) analysis of the deposit as shown in Table 3. The major element found in the deposit is Fe (65%), followed by S (10%), with minor element Ni (<10%) and trace elements of Si, Cu, Cr, Cl, P, Ca and Al. The chemical characteristics of the deposit suggest corrosion

products (Fe, Ni, Cr) and presence of Nalco 9354 (S). The abundance of Fe over Ni in the corrosion products is from corrosion of non-SS316 portions of the surface injection facilities. Unlike the MGPF skid, which is primarily made of SS316 fittings and tubings, the MG-19 skid was composed of combined SS316, SS304 and carbon steel alloy materials. Also the make-up water for injection passes through carbon steel alvenius lines, which can increase Fe in the water phase through low temperature corrosion.

The remaining inhibitor solution (~10% v/v) close to the nozzle tip was collected and sent to the Central Chemistry Laboratory in Manila for standard NACE calcite anti-scalant test. The sample was turbid with very distinct, fine black deposits. Filtered and unfiltered samples were subjected to the NACE standard test method for determining the ability of chemical inhibitors to prevent the precipitation of calcium carbonate from solution. The results of the standard test are shown in Table 4. It is clear, that after prolonged (2 days) exposure to high temperature (>280°C) conditions the inhibitor has virtually lost (only 3-5% remain) its inhibition property (Alvis-Isidro, et al., 2001a). In contrast, the original (10% v/v) Nalco 9354 had a 100% inhibition with the NACE test. Previous thermal stability studies on Nalco 9354 at 280°C for 4 and 2 hours exposure have positively shown thermal degradation with formation of black precipitate (Ramos-Candelaria, 2001). Another laboratory test on Nalco 9354 at 280°C for 10 minutes has already degraded and formed black precipitate (Fig. 8) with an NACE test showing only 20% inhibition (Alvis-Isidro, et al., 2001b). On the other hand, laboratory test at 280°C and 10 minutes exposure of Nalco 9354, which did not form the black deposits, still exhibited a high 90% inhibition (Alvis-Isidro, et al., 2001c). It appears that formation of black deposits for Nalco 9354 is a good indicator of thermal degradation and lost of inhibition.

FT-IR spectra (Fig. 9) of the black deposit show the absence of absorption bands in the 1000 – 3000 cm^{-1} region characteristic of organic compounds. Only a peak at the 600 cm^{-1} region characteristic of $=\text{CH}_2$ groups or $\text{P}=\text{S}$ groups remains. The black deposit is likely the carbonized or charred remnant of the original polymer. The high temperature has completely destroyed the $-\text{COOH}$ groups and the original polyacrylate backbone of the polymer.

Table 4. NACE Tests of Nalco 9354 during thermal stability tests and recovered MG-19 Injectate (~10% v/v) from the tubing.

Sample	%Inhibition	Remarks
Nalco 9354	100	As control sample
From MG-19 CIS (Filtered)	5.03	Cloudy solution
From MG-19 CIS (Unfiltered)	3.35	Cloudy solution with fine black ppt.
Nalco 9354 after TST	89.6	Pale yellow solution, no black deposits
Nalco 9354 after TST	20.6	Cloudy solution with fine black deposits

Notes:

1. TST or Thermal Stability Test conducted at the CCLS Laboratory.
2. Nalco 9354 (5%) subjected to 190°-270°C for 63 minutes and 280°C for 5 minutes. Samples were place in sealed stainless steel tubes (air-free) then underwent programmed heating inside the furnace.
3. NACE test conducted at 70°C for 24 hours using mixture of synthetic brine (~2000 ppm Ca) saturated with CO_2 gas with 10 ppm of inhibitor solution.

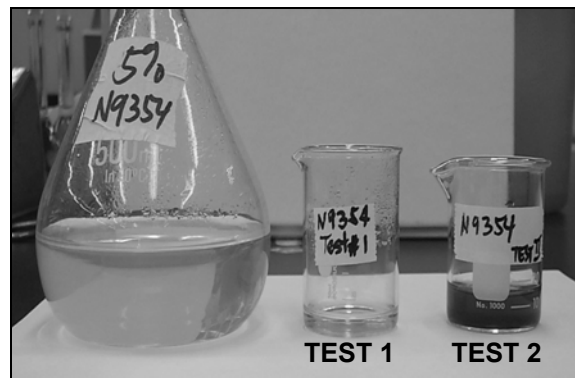


Figure 8. Thermal stability test of 5% Nalco 9354 inside the furnace at exposure temperature of 280°C for 5 minutes (Test 1) and for 10 minutes (Test 2). Note the black deposits formed after only 10 minutes of exposure.

Polyacrylates can form anhydrides with heating at temperatures above 250°C (Koenig, pers com; Morrison and Boyd, 1998). It is also possible to form crosslinks or a gel network with alkaline (e.g. Mg, Ca) or transition metal ions (e.g. Ni, Cu, Fe) and precipitate out (Koenig, pers com.).

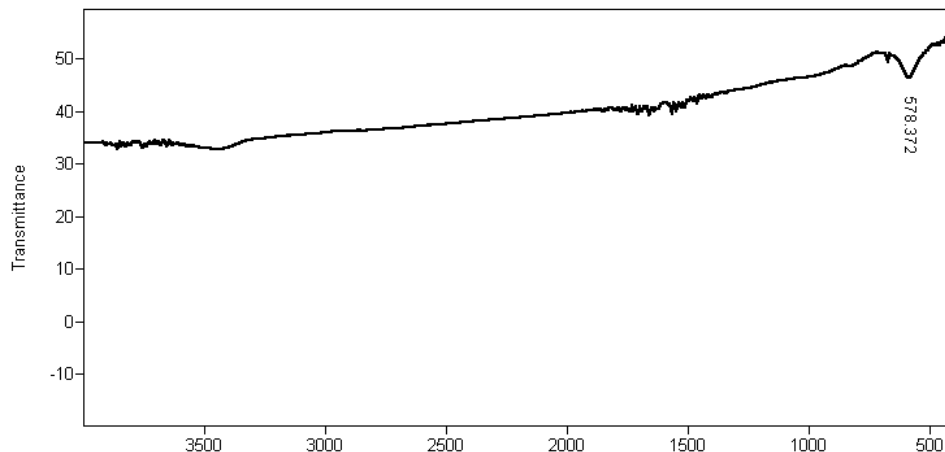
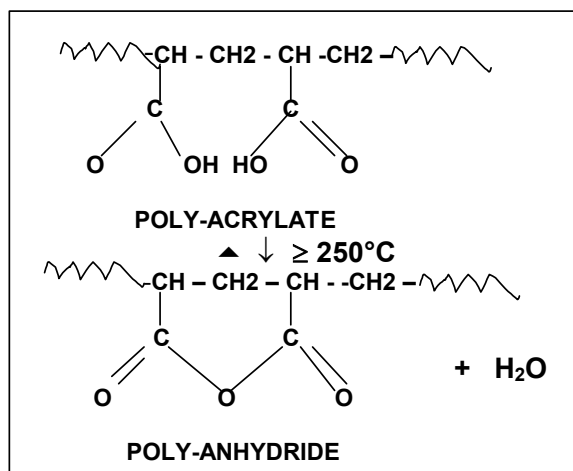


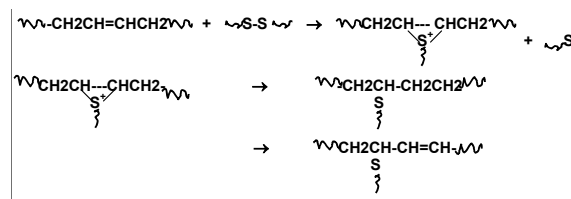
Figure 9. FT-IR spectra of MG-19 CIS tubing blockage showing charred or carbonized polymer, with virtually no remaining organic (C, H, O bond absorption peaks) signature.

Based on the foregoing discussions, the polyacrylates are susceptible to high temperature reactivity or thermal degradation, which destroys their active configuration for inhibition. At temperatures greater than 280°C, the Nalco 9354 formulation is completely degraded and loses its inhibition property. A temperature of 250°C could be Nalco 9354's maximum temperature limit for inhibition. At this temperature the polyacrylate is transformed to its acid derivative or the poly-anhydride (See reaction below). This configuration may not be as inhibiting as the free form long chain polymer. This is because the poly-anhydride is expected to have a more rigid backbone and lesser solubility in water.



Crosslinking is the linking of polymer chains through covalent or ionic bonds (Stevens, 1990). Vulcanization is a general term applied to

crosslinking of polymers using sulfur or sulfur containing compounds. Thermal degradation of the polyacrylate exposes unsaturated bonds or = bonds, where crosslinking can be initiated through the following reaction:



3.0 DISCUSSIONS

Nalco 9354 was the chemical inhibitor of choice for calcite scaling wells at PNO-CEDC due to its very high % inhibition (99-100% with NACE test) and lowest price among surveyed chemicals of its kind (Ramos-Candelaria, 1999). From the very beginning, it was recognized that Nalco 9354 like all polymer based formulations has a tendency for deposition due to: 1) having solubility limits in water of even the most soluble chemicals, 2) evaporation in chemical reservoirs, pumps or tubings of highly concentrated solutions can lead to plugging and absence of inhibition (Ramos-Candelaria, 1999). Its very high density of 1.27-1.32 mg/ml and high viscosity of 51 cps at 60°F is believed to be due to high % composition of the active polymer in the formulation. Nalco 9354 is a clear to pale yellow aqueous solution of an acrylate polymer (~20%), a sulfate and a sodium bisulfate with close to neutral pH (5.4-8.0) of the neat product.

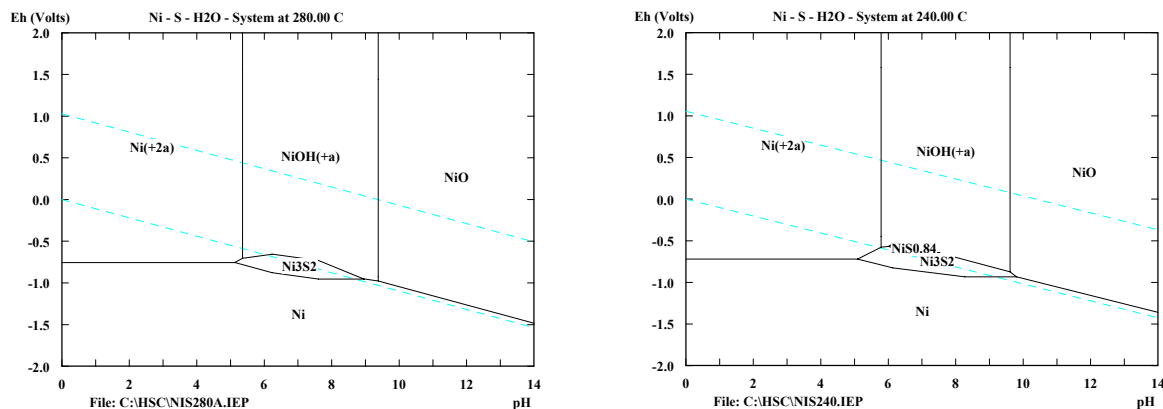


Figure 10. Eh-pH diagram of the Ni-S-H₂O system showing the stability of Ni₃S₂ at the temperatures 280°C and 240°C and in the pH region of the inhibitor solution (pH = 5.5-7) intersecting the lower stability limit of water.

Incidence of Nalco 9354 tube plugging can be explained for wells SP-4D and APO-1D by dehydration and precipitation due to boiling of inhibitor solution. Most of these plugs or blockages occurred near the bottom of tubing close to the dispersion head. Once the plug is formed, it is very hard to dissolve, and the only way to solve the problem is to cut the tubing if the blockage is near the bottom end. Reported incidence of blockages was either preceded by absence of surface injection for a period of time either intentionally (e.g. APO-1D) or due to accidental power interruption (e.g. SP-4D).

For the MGPF wells, where injection temperature is close to 240°C, boiling off and deposition of inhibitor does not result in thermal degradation. The FT-IR spectra remains relatively unchanged denoting intact chemical property or inhibition. Addition of water would re-dissolve this deposit. However, even at 240°C, prolonged exposure (as in the case of SP-4D for more than 2 days), the caked deposit has already undergone thermal degradation. If the deposit were composed of the degraded polyacrylate, this may be re-dissolved by cleaning agents like NaOH in ethanol. However, the deposit also contains high temperature corrosion products (Tables 1 and 2) from the stainless steel tubing (e.g. NiS) which cement and bind with the degraded polyacrylate, making the blockage practically insoluble even by the most aggressive solvent available like fuming HF. The compounding problem with Nalco 9354 is the presence of S as a by-product of the manufacturing process. The presence of S can form additional products with the polymer after

prolonged exposure. With thermal degradation, bond cleavage occurs in the long chain polymer exposing highly reactive unsaturated C groups or = bonds to S. This hot sulfurization process results in the formation of S bridges between carbon chains (Cotton and Wilkinson, 1998) producing a noxious, burning rubber smell. This blockage has been variously described as a black flaky deposit to the more advanced tar-like insoluble mess.

The presence of Fe₂O₃ in the deposits denote the persistence of low temperature corrosion of non-stainless steel portions of the surface injection facilities like alvenius water lines, tubings, gate valves and pressure probes. The presence of clays, rock chips from incomplete filtration of make-up water for dilution, which can block the small diameter capillary tubing, must be addressed by double filtration and/or smaller mesh size filters. The problem of tubing blockage by water contaminants cannot be over-emphasized. After all, one rock chip can stop injection and result in lost of inhibition and the time consuming pull-out.

There is also evidence that the S presence may be responsible for the formation of the nickel sulfide as seen from petrographic identification of deposit (Zaide-Delfin and Rosell, 2001). Preparation of Pourbaix diagram using the HSC program for the Ni-S-H₂O system (Fig. 10) shows predominant stability of the NiS rather than NiO (as identified by Nalco in the deposit) at the temperature and pH of interest.

The formation of black deposition outside the tubing in well MO-2 remains unresolved. The presence of the black deposit above the injection point was believed to be due to excess chemical dosing. However, Nalco claims that the FT-IR spectra of the deposit can also be the signature of oil used in lubricating the tubing.

There is also a reported spontaneous plugging of capillary tubing at MG-19, after only a week of installation without injection stoppage. The very hard, cemented, metallic black deposit cannot be re-dissolved chemically. A few of the black flaky deposits were analyzed by FT-IR but showed mainly the carbonized debris without the usual absorption peaks for intact organic polymers in the 1000-3000 cm^{-1} region. This thermal degradation was the result of long term (more than 2 days) exposure of the inhibitor at temperatures reaching 283°C. Thermal degradation is irreversible and results in complete loss of chemical inhibition property (Table 4).

The polyacrylate dried out at the tip due to the high temperature. The dried polyacrylate also forms an anhydride above 250°C (See reactions in section 2.4). The poly-anhydride is expected to have a more rigid backbone and lesser solubility in water resulting in loss of inhibition. A temperature of 250°C could be Nalco 9354's maximum temperature limit for inhibition. In the presence of excess S, it forms a gel network with alkaline or transition metal ions. The black tar like material formed is insoluble even to the most aggressive cleaning agent.

4.0 CONCLUSIONS

- Plugging of capillary tubings at SP-4D and APO-1D at injection temperatures close to 240°C were caused by temporary stoppage of surface dosing. The absence of high-pressure replenishment from the surface injection facility allowed the inhibitor solution to flow inside the tubing and flash near bottom resulting in the dehydration and precipitation of the inhibitor. FT-IR spectra of the dried inhibitor at 240°C clearly show the absence of thermal degradation
- Prolonged exposure (>2 days) of the dried inhibitor as shown by the SP-4D case even at temperatures of 240°C, already results in

thermal degradation (bond cleavage of the polymer backbone).

- Plugging of capillary tubing in well MG-19 was caused by thermal degradation of the polyacrylate at temperatures above 280°C. Thermal degradation at $T > 280^\circ\text{C}$ results in complete breakdown of the polyacrylate backbone and loss of inhibition property.
- The dried polyacrylate forms an anhydride at temperatures above 250°C. The poly-anhydride is expected to have a more rigid backbone, lesser solubility in water and less inhibition property.
- Nalco 9354 also precipitates by crosslinking forming a gel network with alkaline or transition metal ions. These reactions are enhanced in the presence of sulfur at high temperatures. Nalco 9354 has S as an impurity in the manufacturing process. The black tar like material that is formed by this vulcanization process is insoluble to even the most aggressive cleaning agent.
- There is evidence of high temperature corrosion inside the capillary tubing in the presence of S. Petrographic and thermodynamic calculations (Eh-pH diagrams) have shown the presence of stable NiS product at 240°C and 280°C. In addition Cr_2O_3 , a high temperature corrosion product of stainless steel was also found in the plugs.
- Some plugs were caused by unclean stainless steel tubing and incomplete water filtration where rock chips, corrosion from galvanized surface facilities (e.g. gate valves, tubing, pressure probes) entered the small diameter capillary tubing.
- At Manito, the cause of the black deposition on the outside of the tubing cannot be firmly established by available data.

5.0 RECOMMENDATIONS

- Polyacrylate based inhibitors like Nalco 9354 are recommended for use as a calcite inhibitor in geothermal fields where the injection temperature is $\leq 250^\circ\text{C}$. It cannot be used for Mahanagdong where injection temperatures are already $> 270^\circ\text{C}$.

- For Mahanagdong, evaluate other anti-scalant chemicals, which have thermal stability >250°C. The anti-scalant chemical should have thermal stability, high inhibition (>50% with NACE Test) and low price (must be competitive with yearly work-overs) for it to be commercially viable for Mahanagdong.
- Avoid flashing of the inhibitor solution (Nalco 9354) inside the tubing resulting in dehydration and precipitation of the polymer, by injecting under pressurized conditions.
- Provide back-up power supply (or uninterrupted power supply) to chemical dosing pumps to ensure on-line injection at all times.
- In the design and preparation of injectate solutions, aim for the highest pump flow rate for faster or short residence times of inhibitor in tubing. This will avoid long-standing or stagnant solutions in the line exposed to high temperatures where viscosity, solubility and chemical changes can lead to deposition inside the tubing.
- Use only clean, filtered make-up water for dilution of the neat inhibitor to exclude debris, which can cause plugging of capillary tubing. Install filter systems prior to mixing and after the feed tank prior to the pump skid.

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