Bacman Geothermal Production Field Experiences in Silica Deposition and Control Using Chemical Inhibitors

Almario D. Baltazar Jr, Ramonito P. Solis, Fidel S. See and Anna Cristeta R. Panopio
Energy Development Corporation, Energy Center, Merritt Road, Fort Bonifacio, Taguig City, Philippines
baltazar.ad@energy.com.ph

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ABSTRACT
The Botong Sector of Bacon-Manito Geothermal Production Field is an excellent laboratory for the study of silica scaling for its high silica content and pioneering works on use of antiscalant polymer for the prevention of silica scaling in geothermal system.

The field process set-up has a second flash system that further increased the super saturation of silica to a concentration of 1000-1300 ppm in brine. The brine chemistry was well studied and different approaches to prevent silica scaling were tested including: a) silica slurry injection, b) cold injection scheme with brine treatment using antiscalant, c) hot injection experiments with antiscalant and d) tests with new inhibitor.

The different strategies resulted to successes and failures, difficulties in operation, costs, and largely understanding of silica chemistry and disposal at Botong condition.

Pilot studies on the use of polymers at various conditions showed better success and relatively more efficient system that resulted to a successful 10-year operation of Botong Power Plant.

1. INTRODUCTION
Scaling in pipes due to deposition of silica is a worldwide problem in the geothermal industry. Its major impact is that it limits the development of geothermal resources for electrical power generation. Operationally, this problem can be avoided by maintaining a high separation pressure and flashing only 20-25% of the reservoir fluids into steam. Under this condition, the brine remains unsaturated with silica, such that the silica saturation index (SSI) is less than 1. However, this process requires more production wells to generate the required amount of power. Thus, the development cost is largely increased.

After separation, most geothermal fluids are 10-30% supersaturated with respect to silica. This condition leads to silica deposition in the fluid collection and recycling system (FQRS), injection wells and geothermal reservoir. The silica deposits are usually vitreous to hard porous scales. Cleaning of pipes and injection wells entails substantial cost, which increases the operating and maintenance expenses for power generation.

The Botong sector of Bacon-Manito Geothermal Production Field (BGPF, Fig. 1) in Sorsogon, Philippines is no stranger to the silica scaling problem. Several brine disposal schemes, including low temperature injection, cold injection scheme with brine treatment using antiscalant, hot injection experiments with antiscalant and studies with new inhibitor were field tested, (Solis et al., 1995; Candelaria et al., 1996; Baltazar et al, 1997; Solis et al, 2001; See, 2007; Panopio and Solis, 2010).

2. THE BOTONG COLD OR LOW TEMPERATURE INJECTION SCHEME
Wastewater reinjection schemes during well testing in PNOC-EDC exploration and development areas became necessary due to strict environmental standards. In BGPF, the Botong wells especially OP-3D and OP-4D (Fig. 2) have generated fluids with high silica concentrations. Direct reinjection of waste geothermal brine from these wells posed a serious problem because of a likely deposition of silica along the reinjection lines and inside the well bores of OP2RD.

Field experiments conducted by the Geoscientific Department proved the viability of utilizing low-temperature wastewater reinjection scheme for the disposal of silica-rich brine. The Botong cold or low temperature injection scheme is through gravity injection to a nearby reinjection well, OP-2RD. The separated wastewater came from an elevated cooling pond, allowing the amorphous silica to precipitate as temperature declines to about 40°C (BGSCDC, 1993).

Like the chemical treatment and aging technique applied to the Ohaaki waters in New Zealand, a new problem in the disposal of silica sludge was
foreseen and a task force was created in anticipation of this problem.

Figure 2. Location of wells OP-3D and 4D and RI well OP-2RD at the Botong Sector of BGPF.

3. SILICA SCALE INHIBITION STUDY USING GEOGARD SX

The scaling problem in Botong was abated with the introduction of Geogard SX (GSX) in the disposal system. GSX, a phosphino carboxylic acid copolymer is a product of a three-year (1992-1995) research cooperation between PNOC-EDC and FMC of U.K. After testing several polymers for silica scale control in local geothermal brine, GSX was designed, formulated and successfully tested in the field (Garcia et.al., 1994).

A field trial on the application of an organic additive, phosphino carboxylic acid copolymer, was conducted in an actual geothermal system to evaluate its effectiveness in preventing silica deposition from brine containing ultra high silica concentration (1000-1300 ppm). A low concentration of polymer was applied for about five months, and treatment efficiency based on silica concentrations in various sampling points ranged from 64-98%. Treatment efficiency has improved over time. Massive silica scaling in the fluid collection and recycling system was minimized, while nominal scaling at the separator vessel and gel deposition occurred at the injection pipeline (Baltazar et.al, 1997).

Results also showed that silica scaling on metal surfaces and in sample rock samples can also be successfully prevented in hot injection experiment using GSX-treated brine using OP-4D well. Field test also demonstrated that the polymer can prevent scaling and reduce deposition of soft silica gel in the FCRS and injection well.

The application and effectiveness of GSX in the geothermal system can be controlled and measured. At a low concentration, it effectively inhibits silica scaling. The treated brine can also be disposed through low temperature injection. This is a pioneering technology that promises many applications in other geothermal fields, where conditions are similar.

3.1 The Botong Silica Problem

The Botong brine is unsaturated with silica at the two phase line. At this location, the silica is in the form of molecular silicic acid and probably with negligible amount of silicate anions. At the separator vessel (SV), steam extraction results in a reduction of mass flow at the RI pipeline and a large drop in brine temperature. For Botong system, the separated brine temperature at the SV drops to 165°C and the silica concentration reaches 1000-1300 ppm. This corresponds to a silica saturation index, SSI=1.5 and excess silica above the saturation of about 400 ppm. The large excess in silica can polymerize and produce hard porous deposits along the FCRS.

Further extraction of steam in the second flash vessel (FV) would mean further increase in supersaturation of silica. The colloids in this location are relatively bigger and will normally produce brittle, hard and porous scale under high velocity brine flow. At slow flow rate (i.e. in the thermal pond), the colloids form the non structured gel network which results in the precipitation of soft silica gel. The gel, with time, will form a dense mass of thick, pasty silica at the RI line. At the RI well, the massive silica will be adsorbed and could cause blockages in the porous formations. The net effect is detrimental reduction in the RI well capacity, or at worst, total loss of permeability of the well and the formation.

3.2 Field Set-up

The Botong FCRS and injection system schematic diagram is shown in Figure 3. The GSX injection set-up is located near the OP-4D and OP-3D combined two-phase line. The combined mass flow of the two wells serves as a vehicle for the injected chemical. Prior to the separator vessel, the OP-5D and OP-6D two phase lines meet the OP-4D and OP-3D two-phase lines. Therefore, the combined fluids are already treated before it enters the separator vessel. The brine then passes through a second stage flashing unit, using either the silencer or the flash vessel.

Figure 3. Schematic diagram for the GSX hot injection treatment in BGPF.

Normal operation requires a silencer with a steam trap. The baffles inside the silencer weir box were
made lower than usual, so as to have a continuous
overflow of fresh brine. Brine aging inside the
silencer can then be prevented. The FV-thermal
pond (TP) system serves as a back-up line. The
silencer discharge is then delivered to the mini-TP
(mTP). The mTP has two functions in the system;
1) to trap cuttings and corrosion products, and 2) to
break the turbulence and cool the brine. Cuttings
and corrosion products are major factors in the
cogulation and deposition of silica. Once trapped
in the mTP, the unnecessary debris can be
removed from the system.

The turbulent brine flow turns laminar at the mTP.
The brine temperature also drops to about 70°C.
Thus, flashing inside the RI line is avoided. The
mTP is connected to a deaerator pond (DP) by a
cemented canal. The DP serves as a catchment or
reservoir during high water flow. The brine is then
delivered to the RI well through an 8” Victaulic
pipeline.

3.3 Predicted GSX Action
Geogard SX is an aqueous solution of organic
additive based on phosphino carboxylic acid
copolymer. It is commercially introduced as an
antiscalant. It has dispersive effect toward silica
colloids and is reactive to iron corrosion products.

Dispersants contain balanced hydrophobic
(lipophilic)-hydrophilic functional groups (i.e.
carboxylate-sulfonate-balanced multipolymer) that
enhance adsorption of the dispersant onto colloidal
silica when the temperature is raised. Polymerization is prevented with the dispersant
being adsorbed onto the surface of these “ultimate”
silica particles and impairing a large repulsive force
around the particle to prevent aggregation or
further polymerization. In addition, the enhanced
adsorption of the dispersant at elevated
temperatures is attributed to the removal of
hydration water in the functional groups in the
multipolymer, increasing the driving force for
polymer adsorption (Hann et al, 1993). A
secondary action done by GSX is due to the
presence of a sequestrantr of hydrated iron oxide
(rust). This leaves no reaction site for monomeric
silica to bond with and are, in turn, are handled by
the primary action of the dispersant (Garcia et al,
2000). This action has been confirmed in
laboratory tests at BGPF wherein GSX reacted
with iron to remove the rust. This iron-tolerance
and good dispersant properties is typical of a
polymer that contains sulfonate and carboxylate
groups.

Figure 4 illustrates the predicted mechanism of
the actions of GSX towards colloidal silica and iron
corrosion products.

Figure 4. Predicted Mechanisms of action of GSX
towards silica and corrosion products.

4. HOT INJECTION STUDIES
Studies on GSX-treated Botong brine under hot
injection condition was reevaluated after nine years
of operation (See, 2007). Results of test showed
that the current inhibitor concentration, dosing rate,
brine chemistry, and Fluid Collection and Recycling
System (FCRS) parameters, the predicted
maximum deposition rate is 20 mm per year along
the pipes, and an average of 54 mm per year
inside the well bore. The results indicate that a hot
brine injection scheme is technically feasible.

4.1 Hot Injection Experiment
In 2007, another hot injection experiment was
conducted and yielded promising results. The most
recent test was conducted under the current
operating conditions in terms of brine chemistry,
FCRS parameters and the actual inhibitor dosing
set-up and parameters.

A series of pilot tests were conducted in the field in
order to determine the effectiveness of the current
silica inhibitor under hot injection conditions. A
representative portion of the inhibitor treated brine
was diverted into a series of insulated one-half inch
pipes, with retention vessels connected at the end
of the set-up. The test fluid’s velocity, retention
time, and flow regime were set to mimic the brine’s
characteristics during the actual hot injection
scheme. Results of the latest test showed that at
the current inhibitor concentration, dosing rate,
brine chemistry, and FCRS parameters, the
predicted maximum deposition rate is 20mm/yr
along the pipes and an average of 54 mm/yr
inside the wellbore.

4.2 Deposition Rate
Results of deposition monitoring after 42 days of
testing is shown in Fig. 5. From inspection spool
(IS) #1 to 21, thickness of deposits measured using
a caliper ranged from 0.13 to 2.23 mm. These
translate to projected deposition rates of 1 to 20
mm per year. The highest deposition rate was
measured at inspection spool no. 3 (Figure 6),
located about 125 meters away from the main
brine line and with corresponding measured
temperature of about 128°C. Despite this projected
deposition rate, 20 mm/year, it is still manageable
in actual operation. Based on the present injection
set-up, the brine flow is handled by a 6” diameter
line. So, a reduction of about 1.5 inches in a 10”
diameter line would not affect the line capacity;
regular cleaning of the pipelines could be done
during preventive maintenance schedule.

Figure 5. Sample of pipe with thickest deposit of soft
silica.

Downstream of the test line, away from the main
brine line, the deposition rates obtained were
relatively low despite the significant drop in
temperature. This indicates the effectiveness of the
current silica inhibitor even at such condition. Thus,
a more efficient treatment could be expected at
high temperature and pressure conditions. No
increasing trend in deposition rate along the line
was observed as the temperature of the fluid
decreases and SSI increases, as could be
expected under normal conditions. Again, the silica
inhibitor may have played a role in preventing the
inducing effect of temperature drop in silica
deposition.

The results indicated that a hot brine injection
scheme is technically feasible.

4.3 Deposition Rate In the Retention
Vessels

Significant amount of deposits were formed inside
the retention vessels especially at retention vessel
no. 2 where thickness ranged from 4 to 10 mm
(Fig. 6). Overall, the average thickness in the four
vessels was about 6 mm; this translates to a
projected deposition rate of around 53.5 mm per
year inside the wellbore. However, the significant
amount of deposits inside the vessels were
probably caused by several worst-case conditions
such as flashing due to the abrupt change in pipe
diameter from ½ to 9-inches inside the vessel,
laminar flow, and the significant drop in brine
temperature to as low as 85°C. The atmospheric
pressure at the retention vessel outlet may have
also contributed to additional flashing in this part of
the set-up. During the actual hot injection scheme,
the above scenarios can and should be prevented.

For example expected temperature drop from
separator vessel to the injection well is less than
5°C; flashing along the brine line could be
minimized by maintaining water level at the
separator vessel and by operating the lines at
flooded condition.

Despite the relatively thick deposits observed
inside the vessels, the total amount of deposits
collected after 42 days was only 10 liters (at 0.078
l/s average brine flow). Based on this data, and
using a simple ratio and proportion calculation, 20
kg/s brine (which is the actual brine flow at Botong)
is predicted to produce approximately 22 cubic
meters of silica deposits per year. Assuming that
all of these will form inside the well bore, a 76-
cubic meter injection wellbore (i.e., production
casing plus slotted liners) such as the current
injection well, would take about three and a half
years to fill-up. Since the deposits formed were
relatively porous, the wellbore may continue to
accept brine even as the deposits are forming.
Again, this is assuming worst condition in terms of
flashing and temperature drop. If such worst-case
conditions can be prevented during actual hot
injection, these projected deposition rates is
expected to be much lower.

Figure 6: Retention vessel no. 2

4.4 Summary and Conclusion

The silica inhibitor at the current dosing rate and
concentration, brine chemistry and FCRS
parameters has been shown to be effective at hot
injection conditions with deposition rates estimated
at maximum of ~20 mm per year along the
pipelines and about 53.5 mm per year inside the
wellbore. The higher deposition rates obtained at
the retention vessels could be attributed to
controllable factors such as pressure and
temperature drops, flashing, and laminar flow.
Such factors must be controlled and minimized
during the actual hot injection scheme in order for
the inhibitor to be most effective. Based on the test
results, a hot injection scheme with inhibitor dosing
is a technically feasible option.
5. SILICA SCALE INHIBITOR TESTING
The search and test for another silica scale inhibitor for Botong brine was conducted in 2008 (Panopio and Solis, 2010). A hot injection scheme is being proposed for implementation as a replacement for the existing cold injection system. GSX has already been pilot-tested for the hot injection scheme, with better results than that of the low temperature brine disposal scheme.

Formula 3680 (F3680), a polyacrylic copolymer was tested at varying concentrations from 5-20 ppm using Botong separated brine at 0.70 MPa with about 45% oversaturation with respect to amorphous silica. The new polymer reduces the silica deposition within the cold injection system with an average deposition rates ranging from 1.76 to 2.76 mm/day as compared to 3.98 mm/day for the untreated line. Treating the brine with 10 ppm F3680 achieved a highest inhibition efficiency of 55.86%. Average deposition rate of GSX-treated brine is 1.27 mm/day, which is higher than any concentration of F3680 treated brine. The efficiency of GSX is consequently higher at 68%.

5.1 Chemical Inhibitors and Dispersants
Chemical scale inhibitors under certain conditions can be used to delay, reduce, or even eliminate scale deposition. The silica inhibitors function as: 1) dispersants; 2) anti-precipitants; 3) sequesterants; 4) chelating agents; 5) crystal modifiers or 6) sludge conditioners to name a few and is dependent on the mechanism of silica deposition (Cowan, et al., 1976). Other effects of using organic scale inhibitors were prolonging the induction period (time before precipitation), decreasing rate of precipitation, reducing the final quantity of the precipitates and highly disturbing the silica crystals.

The mechanism in inhibiting silica deposits of the new chemical inhibitor, F3680, is through threshold and lattice distortion as well as by dispersion (Nicolas, pers. comm., 2007). Chemical inhibitors, which are polyacrylic derivatives, not only function as dispersants and sequestering agents but also act as a deflocculant. The polymer appears to form a thin, self-strippable layer on the surface and thus preventing hard silica deposits to form on the surface of the pipe that are hard to clean.

5.2 Pilot Test Set-ups
Figures 7 and 8 show the schematic diagrams of the cold and hot injection system PTF set-ups, respectively. Figure 7 mimics the actual cold section of the reinjection system in Botong except for the location of the dosing point while Figure 8 was designed to proportionally scale down the pipe sizes and brine flows to attain similar fluid regime in the proposed hot injection line that will be constructed, i.e. fluid velocity and travel time of the fluid in the pipe. Both test set-ups is composed of the following parts namely: the dosing system, the mini-separator, the pipeline, the mini-silencer, the inspection spools, the sampling points with cooling coils, thermo wells and pressure indicators, and the retention vessel.

The set-up was tapped from the two-phase line header; the confluence of all production wells in Botong, using a 1-inch line. The dosing pump for the chemical inhibitor was installed before the mini-separator to ensure complete treatment of the brine and avoid silica deposition in the pipeline. Brine separation was duplicated using a mini-separator vessel while thermo well and pressure gauges were installed after the mini-separator for brine temperature and pressure monitoring.

Figure 7. Cold Injection Test Set-up

5.3 Cold Injection Testing
The deposits formed at the open pipe using 10 ppm F3680 are layers of brownish and moderately hard deposits at lane 1 to flaky and brittle upon drying. At lane 2, granular and compact form of deposits was observed while soft and porous type of deposits was observed at lane 3. (Figure 9) Generally, the deposits are poorly formed, have lesser tendency to adhere and can be easily removed. This is the inhibition mechanism of polyacrylic acid based scale inhibitors where the polymer forms a thin monomolecular layer on the surface. This consequently reduced the tendency for the scale to adhere and thus prevents scale deposition. Layers of monomolecular silica are formed upstream of the pipe which further change
to colloidal deposition upon continued binding of the monomers with the adjacent monomeric particles as the brine flows along the pipe. These colloidal particles are generally hydrated and porous in nature.

Another characteristic of F3680 is its ability to cause considerable crystal distortion once crystallization takes place. This distortion prevents dense and uniform deposit as crystal growth occurs.

Figure 9. Characteristics of deposits at the open pipe using 10 ppm F3680: a) layers of thin but moderately hard; b) granular and compact; c) very soft and porous

5.3.1 Deposition Rates
The change in form and structure of deposits can be correlated with the decline in brine temperature along the open pipe. Table 1 shows the range of temperature along each lane of the pipe and the corresponding silica deposition rates.

<table>
<thead>
<tr>
<th>Location</th>
<th>Brine Temp (°C)</th>
<th>Blank (mm/day)</th>
<th>10 ppm (mm/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lane 1</td>
<td>60-83</td>
<td>8.17</td>
<td>2.53</td>
</tr>
<tr>
<td>Lane 2</td>
<td>45-60</td>
<td>4.45</td>
<td>1.53</td>
</tr>
<tr>
<td>Lane 3</td>
<td>35-45</td>
<td>3.50</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Figure 10 shows the relationship of deposition rates with the amount of monomeric silica in the solution. Based on the figure, silica was deposited from supersaturated brine solution with a silica saturation index (SSI) as high as 1.4 at a rate that increases with the amount of monomeric silica in solution. Although blank run and F3680 treated line showed similar trend, deposition rates of F3680 treated line was significantly lesser than that of the untreated line. The linear relation between deposition rate and % monomer is apparent only at blank run; this is due to the absence of chemical scale inhibitor that will hold the silica in solution and slows down the deposition. Treating the line with 10 ppm F3680 reduces the deposition rate at least about 40%. This is typical of threshold mechanism where the weight ratio of threshold active compound to scale-forming component is 100:1. Since the separated brine in Botong contains about 1000-ppm silica, the brine needs about 10 ppm of the chemical inhibitor to hold the silica in solution.

Figure 10. Deposition rates vs. % monomer

It is observed from the deposits formed along the open pipe that precipitation occurs much more slowly from the solution when the aqueous silica is in the form of polymers rather than as monomers, as evidenced by the decline in thickness of the deposits. Accumulated deposit thickness at the pipe declined from lane 1 to lane 3. This implies that the deposits formed immediately after flashing from the mini-silencer is in monomeric form. Lane 1 has the highest tendency to form solid and moderately hard scale (not gel type) because it has the highest percent of monomeric silica in solution. Ageing the brine by allowing it to pass lanes 2 and 3 of the open pipe allows the silica to be converted to polymerize form, which is weakly flocculated, and gel-type. Since much of the silica has deposited upstream (lane 1) and the brine downstream is already silica depleted, deposition rates will consequently decline in lanes 2 & 3.

5.4 Hot Injection Testing
Yellow slurry-type of samples was collected from the retention vessel after 27-day testing was completed. The type of deposits collected from the vessel is non-adhesive to the pipe wall that can be easily flushed out with pressurized water. Figure 5 shows the picture of the deposits immediately after opening the vessel. The elemental composition of the sample taken from the collected slurry in the retention vessel based on EDX analysis are composed mainly of As (~50%), S (~20%), Si (~10%), and O (~20%) with trace amounts of Ca and Sb.
5.4.1 Deposition Rates

The rate of deposition along the test pipeline ranged from 5 to 150 mg/day (Figure 11). Based on the results, the highest deposition rate of 150 mg/day was measured at the spools installed between 244-250 m away from the mini-separator. The deposits are highest in this area probably due to the flow regime of the brine along the pipelines. Based on the layout of the pipes, there are more bends in this section, probably causing higher system pressure loss leading to scale deposition (see discussion below). As expected, the lowest deposition rates with very thin deposits were found at the hottest portion of the PTF closest to the mini-separator (first 175m). The deposition rates here ranged between 5-30 mg/day at temperatures between 120°C- 160°C.

Line pressures generally follow the temperature trend. The highest drop in pressure (6 MPaa) was noted at the same area were the deposition rate was highest. This section corresponds to the span with the highest temperature drop, since the brine velocity decreased due to the decline in flowrate as an effect of increased number of bends in the pipe layout. This portion of the PTF (120°C) mimics the worst condition within the hot reinjection line, where brine is subjected to further flashing due to pressure drop with a corresponding temperature drop of 45°C from the separation temperature of 165°C (Fig.13).

The measured deposition rate at this portion is 150 mg/day or 55 g/yr. Deposition rate was measured by weight method unlike previous silica inhibition testing that used thickness of deposits, as basis for the deposition rate measurement due to the fact that the deposits formed during this test was soft and non-adherent to the pipe. Minimal coating of deposits was present along the pipelines.

5.5 Silica and Chloride

The silica concentrations at the different sampling points in the cold injection set-up showed erratic results indicating that the brine is not homogeneous and that polymerization has occurred at different molecular weights/lengths. Consequently, samples containing longer chains will give higher concentration. However, the decline in total silica at the end of the set-up of >200 ppm is apparent (Figure 14). This translates to the amount of silica that deposited along the line.
**Figure 14. Profile of Total Silica in Cold Injection Set-up**

Chloride concentrations at the different sampling points showed more stable results except for the 10-ppm F3680 concentration. The deviations are due to fluctuating brine flow rate.

On the other hand, approximately 100-mg/L drop in total silica was measured along the whole length of the hot injection test pipes. Similar with the cold injection testing, the fluctuation in the silica concentrations during the duration of the testing indicates that the brine is not homogeneous which is also consistent with the Cl concentration trend (Figure 9). The variation in silica concentrations is due to the fluctuations in the temperature causing polymerization of silica to occur at different molecular weights/lengths. The brine homogeneity is hard to maintain because of the fluctuating brine flow at the source and low brine flow rate flowing in the pipe (~0.039 kg/s).

**Figure 9. Chloride trend in Hot Injection Set-up**

**5.5 Summary and Conclusion**

- F3680 is effective in controlling silica scale formation in both the cold and hot injection scheme in Botong.

- Average deposition rates using 10 ppm F3680 in cold injection testing is 1.76 mm/day as compared to untreated line, which is 3.98 mm/day.

- Deposition rates are highest immediately after the brine flushed from the mini-silencer where monomeric silica is highest at this portion of the pipe. Rate of deposition consequently declines as the brine cools downstream.

- Brine treated with F3680 produced poorly formed, layered, thin but moderately hard silica deposits, to granular and compact and finally soft gel type that can be easily removed.

- Deposition rates in hot injection testing were as low as less than 30 mg/day (11 g/year) at the hotter portion of the PTF (120-160°C). At the worst condition of the PTF (45°C drop from the separation temperature of 165°C) however, higher deposition rates were measured, with maximum recorded at 150 mg/day (55 g/year).

- Brine treated with F3680 produced yellow slurry and deposits that are less adhesive to the pipe wall. This type of deposit can easily be flushed out with pressurized water.

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