SUCCESSFUL USE OF PRODUCED WATER DISTILLATE AS FEEDWATER FOR HIGH PRESSURE DRUM BOILERS.

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ABSTRACT

The steam assisted gravity drainage enhanced oil recovery process (SAGD) requires large amounts of high-pressure steam. Virtually all the steam is injected downhole to stimulate oil production so the boilers operate on 100% makeup water with no condensate return. Water separated from the recovered oil, so called produced water, is the source of the boiler feedwater. Produced water contains high concentrations of salt, hardness, alkalinity and silica. Without extensive pretreatment it would be unsuitable for operating high-pressure drum boilers. This paper gives two examples of successful operation of high-pressure drum boilers on produced water that is pretreated by evaporation. Both systems use mechanical vapor recompression evaporators to produce a distillate of sufficient purity for direct application as boiler feedwater. One system uses an all-polymer internal treatment program that has produced clean boilers that operate at a very low corrosion rate. Indeed, we discuss subtle changes in the iron release caused by the use of different burners in otherwise identical boilers that would have been undetectable if the boilers were not operating under such remarkably stable conditions. The second example is a system that operates sophisticated high efficiency boilers and gas turbine electric generators with heat recovery steam generators with 100% produced water distillate feedwater. These boilers use a buffer phosphate internal treatment program that is particularly easy to apply and control because of the consistency of the produced water distillate.

INTRODUCTION

Thermal oil recovery operations such as steam assisted gravity drainage, SAGD, use water separated from the produced oil to generate steam that is injected into the oil formation. The produced water is of low purity and generally requires pretreatment before it can be used as boiler feedwater. Simple softening techniques such as lime softening or resin ion exchange can be used to remove hardness and/or silica to make the water suitable for use in once-through steam generators (OTSGs). The OTSGs have certain design aspects that allow them to produce wet, high-pressure steam with relatively impure water. However, OTSGs have lower heat transfer efficiency than conventional drum boilers and require regular mechanical cleaning, a process known as pigging. OTSGs also boil a lower percentage of the feedwater. OTSGs vaporize 70%-90% of the boiler feedwater with the rest remaining as liquid droplets entrained in the flowing steam. Sometimes this wet steam is injected directly into the oil formation but more often liquid water is separated and recycled in some manner or disposed of as waste. In contrast, drum boilers have higher thermal efficiency, require much less frequent or no cleanings and vaporize 96-98% of the feedwater. Not only are drum boilers more efficient from a thermal and water balance standpoint but they are generally more readily available and less capital intensive.

Drum boilers require a higher purity feedwater than OTSGs so simple softening techniques are insufficient to prepare the boiler feedwater. Evaporators that operate by mechanical vapor recompression are commonly employed to produce this higher quality feedwater. (Beesley, Rhinesmith 1980; Yundt 1984) The evaporation process separates all non-volatile impurities from the produced water with very high efficiency producing water suitable for use in conventional drum boilers. The water produced by evaporation is called distillate. There are some differences between using distillate as boiler feedwater and

feedwater produced by more typical techniques such as resin demineralization/decarbonation or reverse osmosis. The evaporation process can sometimes be more prone to upset conditions caused by foaming or other mechanisms that cause entrainment of concentrated water from the evaporator sump into the distillate. The produced water source is also more likely to contain volatile impurities such as H₂S and NH₃ that are not completely removed by evaporation that must be considered when operating the units.

Another consideration for boiler treatment stems not from the chemistry of the feedwater but the operation of the SAGD process itself. Most industrial boilers are used in plants that have variable steam load such as paper making, oil refining or chemical processing. In those industries plants are generally constructed with excess steam generation capacity and boilers must often swing steam generation load. The variable steam generation burden is commonly split between base load boilers and swing boilers. Thusly, the vast majority of industrial boilers are rarely operated at their maximum steam capacity. In contrast, SAGD is a more stable process where a constant steam load is generated for many months on end and where changes in steam load are either caused by planned maintenance outages or unexpected mechanical problems with the system. Indeed, there is a great incentive to produce the greatest amount of steam possible from each boiler since that is the most capital efficient operation mode and because every kilogram of steam that is generated produces the end product of the system, crude oil for sale. It is often difficult to determine, a priori, the maximum output of a boiler and when boilers are operated at their maximum output the natural circulation of fluid in the boiler is at the edge of the zone where steam stratification can occur. Circulation deficiencies can cause corrosion problems like caustic gouging so the boiler treatment must take that into consideration. Treatment programs for drum boilers in the SAGD process must minimize free hydroxide alkalinity to reduce the danger of caustic gouging corrosion. Upsets that introduce entrained droplets of sump water into the distillate bring NaOH along with them since most evaporators are operated at a high sump pH.

All boiler treatment programs should supply a reserve of alkalinity to protect against low boiler water pH that might be caused by acidic compounds entering the boiler water. The entrained NaOH in the distillate is sometimes inconsistent and can be insufficient to supply the desired reserve alkalinity. Supplemental feed of small amounts of NaOH can be used. A safer approach is to supply the alkalinity reserve with a chemical that does not deliver free hydroxide to the system. Lower volatility amines where a useful portion of the chemical remains in the boiler water have been used successfully to supply alkalinity reserve for all-polymer boiler internal treatment programs. More standard buffer phosphate programs are applicable to evaporator distillate with low hardness. Hardness concentration is the second major consideration for treating boilers operating on produced water distillate. Entrained sump water also brings along Ca and Mg hardness so distillate rarely has the same hardness concentration as feedwater prepared by resin demineralization. Treatment programs must take this into account to prevent hardness scale deposits from forming on the boiler heat transfer surfaces. Fortunately, boilers in the SAGD process operate at pressures where synthetic polymers are thermally stable enough to provide good scale inhibition. Drum pressures commonly range from as low as 4200 kpa (600 psig) up to around 10500 kpa (1500 psig). All polymer programs are useful in most of this range and polymer overlays are effective over the entire span of pressure/temperature. Higher hardness concentrations generally require the use of an all-polymer program. All-polymer programs can handle very high hardness concentrations, over 1 ppm as CaCO₃ in the boiler feedwater. Calcium phosphate sludge can form in boilers operating on buffer phosphate programs if there is significant hardness in the feedwater. Antiscalant polymer overlays are needed in these systems. If average hardness concentration is below about 50 ppb as CaCO₃ good performance can be obtained with buffer phosphate programs that include a good antiscalant polymer.

SITE 1: IRON PICKUP IN DRUM BOILERS TREATED WITH AN ALL-POLYMER PROGRAM

The first site we will discuss operates 5 "O style" package boilers with a drum pressure of 6000 kpa (870 psig). All the boilers are identical from a tubing standpoint and are operated exactly the same in terms of steam output and cycles of concentration. However, boiler 4400 is relatively new compared to the other 4 boilers and is equipped with an ultra-low NO_X burner. The site supplements produced water distillate with brackish well water treated by reserve osmosis to create the final boiler feedwater. (Breland, Godfrey, 2017) This allows the evaporators to run at a steady output that produces particularly pure distillate and the RO processed supplemental water supplies a small amount of alkalinity. Between the alkalinity supplied by the RO water and the small amount of NaOH carryover in the distillate the final boiler feedwater has the perfect amount of alkalinity to run an all-polymer program with a minimal concentration of free hydroxide in the boiler water. The program has been very successful with no significant deposition noted in the boilers. No hardness scale has been observed in the boiler deposits which are almost pure magnetite (92%) with a small component of silica (2%), and the balance of the deposit comprising trace quantities of aluminum, sulfur and organic compounds.

The boiler feedwater chemistry is depicted in Figure 1. The conductivity is largely due to the presence of volatile components such as H_2S and NH_3 not removed by the evaporator. These components go with the generated steam and have not been observed to cause problems in the system. The blowdown conductivity is actually less than the feedwater conductivity for this reason even though the boilers operate at about 35 mechanical cycles of concentration. Average boiler feedwater chemistry is listed in Table 1.



Figure 1. Feedwater chemistry over time at site 1.

Average Boiler Feedwater Chemistry			
Conductivity	191 uS		
Hardness	23 ppb as $CaCO_3$		
Fe(II)	6.5 ppb		
SiO ₂	52 ppb		
рН	9.55		

Table 1. Average boiler feedwater chemistry at site 1.

The internal treatment program in use is an all-polymer program. Table 2 shows that the boilers do maintain a reasonable alkalinity reserve at a relatively low boiler water pH. This site has gone to great efforts to maximize steam output from the boilers while minimizing NO_x content of the combustion gas. One attempt to produce maximum steam generation resulted in steam stratification and a caustic corrosion failure in one tube. The tube was near the rear end of the firebox and the failure was just after a bend in the tube that brought the vertical generating section of the tube into a more horizontal roof tube orientation that sent the fluid towards a junction with the steam drum. This was exactly where a failure from slight overfiring would have been expected. The vertical generating section of the tube was in the hottest part of the firebox and the bend gave the steam the opportunity to stratify. After consultation with the manufacturer most of the refractory insulation on the floor of the firebox was removed to decrease firebox temperature and reduce NOx production. This modification also redistributed steam generation and circulation in the boilers. The same steam output was maintained after this modification but the increased steam production in the floor redistributed flow in the boiler and prevented the steam stratification noted in the roof tube. The floor modification worked quite well for about 5 years at which time steam leaks were noted from a few circumferential cracks on the top of some floor tubes. The cracks resembled fatigue failures and loose magnetite was noted on the bottom of the floor tubes. We feared that the fatigue failures might have indicated a slight overheat in the floor tubes. However, metallographic analysis showed no indication of overheat in the microstructure of the steel near the cracks. The boiler had suffered a significant number of burner trips, which is not uncommon at SAGD sites since the various unit processes are highly integrated and the sites are often rapidly expanding and installing new equipment. Since the boilers are always operated at maximum steam output trips cause the maximum thermal stress possible on the tubes and it would appear that the repeated stress from the steam quenching process was responsible for the fatigue cracks in the floor tubes. The roof tube at the steam stratification site had never perforated in this boiler but was sampled during the floor repair. The tube had clearly suffered some gouging damage before the floor refractory insulation was removed but the old damage had repassivated very convincingly. It would appear that the floor refractory modification was quite successful in producing a better balance of steam production in the firebox preventing the steam stratification while maintaining a very high maximum steam output rate.

Average Boiler Blowdown Chemistry					
Boiler	4100	4200	4300	4400	4500
рН	10.0	10.1	10.1	10.1	10.1
ALK ppm as $CaCO_3$	46	46	47	47	46
Fe(II) ppb	48	48	48	143	49

Table 2. Blowdown chemistry of the boilers.

Routine colorimetric soluble iron testing is performed on all five boilers. (Godfrey, Chen, 1995) The soluble iron concentration has been extremely stable over the long term in the blowdown of four boilers. The four boilers have identical concentrations of soluble iron in their blowdown. The floor cracks were noted in one of these boilers but the soluble iron numbers certainly gave no indication of that corrosion reaction although that may be reasonable since the corrosion product would be solid magnetite and most of it probably stayed in place. Interestingly, the newest boiler has roughly three times the concentration of soluble iron. This is not a passivation effect. The boiler has been in use for over a year and the iron values have been stable for many months. Addition of extra passivating oxygen scavenger to the system has no effect on the soluble iron values.

Despite our efforts we cannot claim to interpret these differences but we do find them quite intriguing. The magnitude of these values is not unusual. In fact, all the concentrations are at the lower end of the range expected for boilers operating on all-polymer treatments. Even ignoring iron in the feedwater 143 ppb iron in the blowdown would only amount to about 3kg loss of iron from the boiler per year in a unit that weighs on the order of a hundred tons so it does not necessarily represent significant corrosion. The only real difference in the design or operation of the units is the ultra-low NO_X burner which does represent a significant change in the pattern of heat input to the boiler and a concomitant change to the detailed circulation pattern. This boiler also contains slightly different attachment brackets for items in the steam drum that appear to be alloy steel and may be producing some galvanic corrosion products although no visible damage is evident.

SITE 2: CONGRUENT PHOSPHATE TREATMENT OF BOILERS OPERATING ON PRODUCED WATER DISTILATE

This site operates three high efficiency drum boilers and two gas turbine heat recovery steam generators on 100% produced water distillate feedwater. Feedwater purity over time in terms of conductivity and total hardness is shown in Figure 2. Average conductivity is 77 uS and average hardness is 35 ppb as CaCO₃. The cation conductivity of the distillate is 30-40 uS so there is a significant contribution of volatile components including H₂S and NH₃. The volatiles have not presented any detectable problems for the system and should be partially removed by deaeration prior to the boilers. The normal hardness recommendation for a buffer phosphate program would be <20 ppb as CaCO₃. The average hardness is somewhat higher than this recommendation and there are short spikes above 100 ppb. The treatment program has not suffered noticeably from this hardness in terms of phosphate consumption or deposit formation. The target phosphate concentration in the boiler water, 12.5 ppm as PO₄, is high enough to absorb the hardness without major changes due to phosphate consumption and sufficient dispersant polymer is present in the treatment product to prevent deposition of sludge or scale.



Figure 2. Boiler feedwater (produced water distillate) purity.

The congruent phosphate program operates by supplying a phosphate buffer to the boiler water. (Flynn, 2019) It is controlled by evaluating a plot of boiler water pH versus phosphate. The ideal position for this buffer is a sodium to phosphate ratio of 2.6. If the ratio is greater than 3.0 free hydroxide is present in the water and presents a risk of caustic gouging corrosion on the boiler tubes. If the ratio is less than 2.2 there is a risk of another type of corrosion called acid phosphate corrosion. The goal is then to keep the sodium to phosphate ratio in the 2.2-3.0 range. Figure 3 presents a typical control chart for evaluating the congruent phosphate treatment program at this site. The solid lines represent sodium to phosphate ratios. The top red line is 3.0 sodium to phosphate ratio of 2.2. The individual points in these control graphs represent measurements of boiler blowdown grab samples color coded for the five individual boilers taken over time. It is apparent from the figure that overall operation is quite good since almost all the points are within the target sodium to phosphate range with only a few points falling just outside the range. This sort of operation is easy to control when the evaporator is running steadily, however, there are periodic procedures that cause both the spikes in the conductivity and hardness of the feedwater but also upset the good control of the congruent phosphate program.



Figure 3. Typical congruent phosphate control chart for the system

The spikes in feedwater conductivity and hardness are associated with compressor blade washes. Mechanical vapor recompression evaporators use turbo fan compressors to compress and heat the evaporated water vapor so that hot gas can be used on the shell side of the evaporator tubes to drive the evaporation process. (Beesley and Rhinesmith, Yunt) If droplets of entrained sump water are not completely removed by the mist eliminators prior to the compressor the impurities present in these droplets can deposit on the fan blades as a solid material. Eventually, this deposition can cause vibration in the fan. The deposits can be removed by this wash but the wash water can be partially incorporated into the distillate contaminating it with the material that deposited on the fan blades. The contaminants are mainly salts such as NaCl which increases distillate conductivity but fan blade deposits also contain hardness as well as NaOH since the evaporator sump is at a high pH. The NaOH makes the biggest impact on the boiler treatment program.

Figures 4 and 5 shows the impact of a blade washes on the congruent phosphate program. The numerous points inside the control range were obtained before the blade wash. The points outside the control ranges were taken immediately after the blade wash. The NaOH released to the boiler feedwater drives the sodium to phosphate ratio higher and results in the points above the control range. The control response to this non-conformance is to increase the boiler blowdown rate which reduces the phosphate concentration unless the treatment product feed rate is increased to compensate for the higher blowdown rate. Increasing blowdown does eventually correct the problem but it is a fairly significant waste of water and adversely affects plant water balance.



Figure 4. In specification operation prior to a blade wash and out of specification chemistry immediately after compressor blade washing.



Figure 5. Another example of the effect of a blade wash on boiler water buffer chemistry

Since the blade wash contamination injects NaOH into the system the phosphate treatment product can be modified so that its buffer position is changed giving the buffer more capacity to absorb NaOH. Two different phosphate products with different sodium to phosphate ratios were fed to two identical boilers. Table 3 shows that operation in the control ranges was possible at higher cycles of concentration, meaning significantly less blowdown, when using a lower sodium to phosphate ratio product.

Phosphate Products with Different Na/PO ₄ ratios					
Boiler Water Conductivity 500 uS					
Na/PO ₄	Average BD pH	Cycles of Concentration			
1.67	9.79	28			
1.0	9.89	40			

Table 3. In specification operation possible at higher boiler cycles of concentration using a phosphate buffer product with lower sodium to phosphate ratio.

Efforts were also made to improve the procedures for the blade washes. After useful discussions with the evaporator manufacturer new procedures are being evaluated. As of this writing initial results seem encouraging. Figure 6 shows an operational period that included five blade washes. Boiler H720 is operating on a phosphate product with 1.0 sodium to phosphate ratio at 50 cycles of concentration which is our ultimate goal for that parameter. The other four boilers are operating in the control range during blade washes in the range of 42-45 cycles of concentration on a phosphate buffer product with a 1.67 sodium to phosphate ratio.



Figure 6. Boiler water buffer chemistry during five blade washes with improved procedure.

CONCLUSIONS

Site 1 has successfully operated drum boilers on produced water distillate for many years on an allpolymer internal treatment program. Addition of RO pretreated brackish water as a supplement to the produced water distillate has expanded capacity for the addition of new boilers and created a feedwater blend with nearly ideal alkalinity for an all-polymer program. The boilers have never experienced hardness scale formation or significant deposition of any kind. Efforts to maximize steam output have resulted in some painful failures but it would appear that the true maximum output of the design is well known at this point. Differences in Fe(II) concentrations in the blowdown of the different boilers are hard to interpret but may be linked to the use of an ultra-low NOx burner which may modify the circulation to some degree.

Site 2 has operated successfully on 100% produced water distillate for many years using a congruent phosphate internal treatment program. Hardness somewhat higher than recommendations has not caused problems with phosphate program control or scale/deposit formation in the boilers. Stable operation in the phosphate control range at 50 cycles of concentration in the boiler water has been achieved through judicious choice of the sodium to phosphate ratio in the treatment product and improved procedures for evaporator compressor blade washes.

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