PEER REVIEWED

A critical review of the use of fireside additives for deposit control in kraft recovery boilers

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ABSTRACT

Various additives can control fireside deposit accumulation in recovery boilers. Results are not conclusive due primarily to the high "ash" content of the black liquor, the high alkali content of the deposits, and the small amount of additives used. Most additives work using these mechanisms: dilution, combustion catalysis, or cleavage plane formation. None of these can satisfactorily explain how a small amount of additive can alter deposit properties. Additives should have no direct impact on fume deposition in the generating bank and economizer due to the low temperatures. Laboratory and field studies suggest that MgO and $Mg(OH)_2$ may control carryover deposition in the superheater region, but they require application in large amounts and effective delivery to the tube surface. Among the common additives, these Mg compounds also cause the least side effects in the recovery cycle because of their extremely low solubility in alkaline solutions.

Application:

A sponging mechanism with the cleavage plane formation mechanism may explain the functioning of fireside additives.

FIRESIDE ADDITIVES HAVE HAD wide use in oil- and coal-fired boilers to reduce the tendency to form deposits and the corrosiveness of fly ash (1, 2). They are usually a mixture of high melting point materials such as MgO, CaO, SiO2, and Al2O3. Minerals such as calcite (CaCO3), magnesite (MgCO3), dolomite (CaCO3×MgCO3), brucite (Mg(OH)2), kaolinite (2SiO2×Al2O3×2H2O), wollastonite (CaSiO3), talc, and vermiculite have also had use.

Additives supposedly help minimize deposit accumulation by:

- Increasing the deposit melting temperature
- Reducing the concentration of low melting point compounds in the deposit
- Decreasing the deposit strength for easier removal of deposits by sootblowers.

In oil-fired boilers and gas turbines, MgO additives (MgO and $Mg(OH)_2$) are effective in reducing fouling and corrosion especially when burning fuel oils containing high concentrations of sulfur, alkali, and vanadium. In coal-fired boilers, additives are not as effective due to the much larger ash content in coal compared with oil—more than 100 times. The amount of additive used is usually insufficient to alter the overall composition of coal ash markedly. The additive nevertheless manages to decrease deposit forming of the ash.

Copper oxylchoride and copper sulfate have had use in coal-fired boilers as a nucleating-enhancing agent to combat slagging problems at the furnace bottom *(2)*. These additives probably induce crystallization in the surface layer of the silicate particles in the bottom ash. The resulting crystalline phase drastically increases the particle viscosity. This prevents coalescence of the deposited particles by viscous flow. SO_3 producing additives such as H_2SO_4 and $(NH_4)_2SO_4$ are frequently used to reduce the electrical resistivity of fly ash particles for easier capture by electrostatic precipitators.

Results observed with some additives in utility boilers led to their use in recovery boilers *(3, 4)*. A survey of recovery boiler operations and plugging in Canada *(5)* revealed that additives had frequent use in the past. Most people stopped using them because of inconclusive results. In some boilers, additives seem to work so well that they have have been used for many years. In other cases, additive treatment was abandoned after a short trial period.

Recent additive application in a recovery boiler in Canada showed that injection with air of a small amount of $Mg(OH)_2$ water slurry into the superheater region helped increase time between boiler washouts *(6)*. Without the additive, the draft loss across the generating bank inlet increased steadily. It stabilized shortly after initiating the additive treatment. Despite the small amount used, the results obtained by using this additive are convincing and seem reproducible. This positive experience has sparked a renewed interest in the use of additives for plugging control in recovery boilers.

More myths than facts presently exist concerning the merits or lack of merits of additive treatments in recovery boilers. Use of additives has generally met with much skepticism and cynicism due to a lack of understanding about what the additives are, how they work, and concerns over the side effects additives may cause in the recovery cycle.

This paper examines several types of additives commonly used in recovery boilers, how they work, and what potential side effects they may cause.

WHAT ARE ADDITIVES?

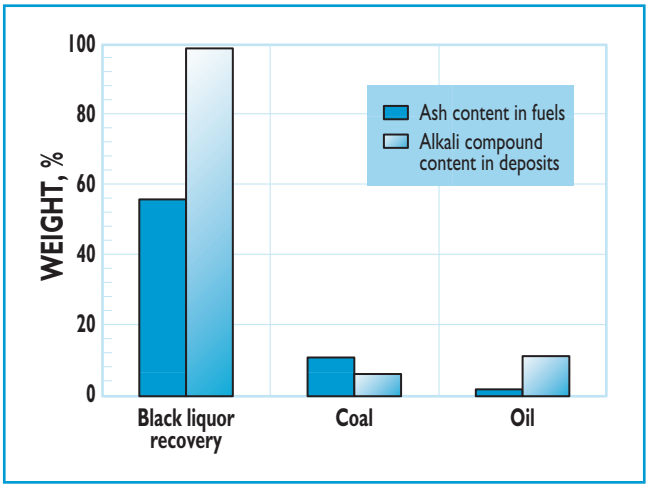
Except copper compounds and SO_3 producing agents used in coal-fired boilers, virtually every type of additive used in utility boilers has been tried in recovery boilers. The additives are typically a mixture of high melting temperature compounds with or without "proprietary" ingredients. Due to their success in utility boilers, Mg, Ca, and Mn additives—singly or as mixtures of MgO, $Mg(OH)_2$, CaO, $Ca(OH)_2$, MnO_2 and silicate minerals—have common use.

Additives used in recovery boilers can be liquid or solid. Liquid additives are usually directly added continuously into the black liquor mixing tank or into the black liquor line at a dose of 0.1–0.5 g of additive per kg of black liquor solids. Solid additives—"as is" or as an aqueous slurry—are applied continuously or on an intermittent 4–8 h basis depending on the severity of the deposition problem. They are usually injected with air into the boiler at an elevation above the liquor guns or into the superheater region. They may also be sprayed through soot-blowers in the superheater region. The dosage rate of a solid additive is typically about the same as for a liquid additive.

WHY ARE ADDITIVES LESS EFFECTIVE IN RECOVERY BOILERS?

The main reason is the high "ash" content of black liquor and the high alkali content of the deposits. Compared with oil and coal, black liquor has a much higher ash content—more than 50% by weight on dry solids. Oil contains <0.1% by weight ash, and coal typically contains about 10% ash by weight. The ash content may vary from less than 2% by weight for anthracitic coal to greater than 50% by weight for high ash lignite coal *(7)*.

Deposits in coal- and oil-fired boilers are typically a mixture of oxides, e.g., SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, K_2O, Na_2O, and V_2O_5 with small amounts of water-soluble alkali compounds, e.g., Na_2SO_4, K_2SO_4, and NaCl. By contrast, recovery boiler deposits consist of almost 100% water-soluble alkali compounds—Na_2SO_4, Na_2CO_3, a small amount of Na_2S, NaCl, and potassium salts *(8)*. Alkali compounds are more troublesome due to their lower melting temperatures and lower viscosities and surface tensions when they melt.



1. Typical ash content in fuels and alkali compound content in deposits in recovery, coal-fired, and oil-fired boilers

Figure 1 compares the composition of recovery deposits to that of utility boiler deposits. The large quantity of ash and the high concentration of alkali compounds make modification of the thermal characteristics of recovery boiler deposits more difficult than those of oil-fired and coal-fired boiler deposits. For an additive to be effective in a recovery boiler, a larger amount is therefore necessary. This is highly undesirable not only because of the additive cost but also because the recovery boiler "ash" must be reclaimed as cooking chemicals. A large dosage of additive inevitably contaminates the ash.

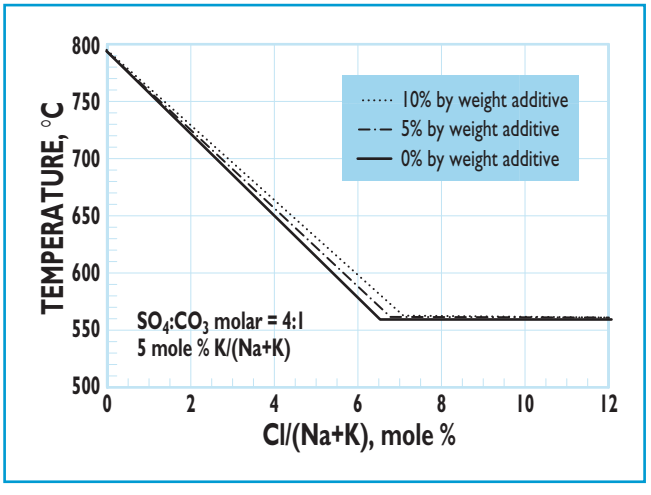
HOW DO ADDITIVES WORK?

Additives used in recovery boilers work by decreasing the concentration of low melting point compounds in the deposit. This makes the deposit less sticky, decreases the deposit strength, or both for easier removal by soot blowing. Depending on the claim by which they supposedly work, additives may have three classifications.

Dilution

This type of additive can be any compound or mixture of compounds that has a high melting point. The additive works as a dilution agent to decrease or "dilute" the molten phase in the deposit. This makes the deposit less sticky and more readily removable by soot-blowers. Although the dilution effect occurs in oil-fired boilers where the ash content is small, it will probably not work in recovery boilers.

Consider a case in which a solid additive is injected with air at a mass flow rate of 10 kg/h into a recovery boiler that burns 75,000 kg/h (4 million lb/day) of black liquor dry solids. The amount of precipitator dust, i.e., carryover plus fume, is typically about 5% of black liquor dry solids or 3750 kg/h. Of this amount, carryover of physically entrained smelt particles accounts for less than 5% or 190 kg/h. In the superheater region, the amount of carryover can be 2–10 times (380–1900 kg/h) higher depending on location since the boiler tubes have not yet screened it.



2. Effect of a hypothetical additive on the sticky temperature of a superheater deposit containing 20 mole percent CO_3/ (Na_2 + K_2) and 5 mole percent K/(Na + K) as a function of chloride content

If we further assume that only carryover (no fume) is present in the superheater region and that the additive is well mixed with carryover deposits, then the additive content in deposits is about 0.5%–3% by weight.

In practice, the concentration of additive is much lower than this because deposits consisting of carryover and fume and additive particles are solid. Deposits do not readily capture them. For additives that have a very fine particle size of <1 μm, the concentration is even lower since small particles follow the flue gas to the precipitator. Chemical analysis of deposits from various recovery boilers using additives has confirmed this. The additive content in deposits and precipitator dusts rarely exceeds 0.05% and 0.2% by weight, respectively.

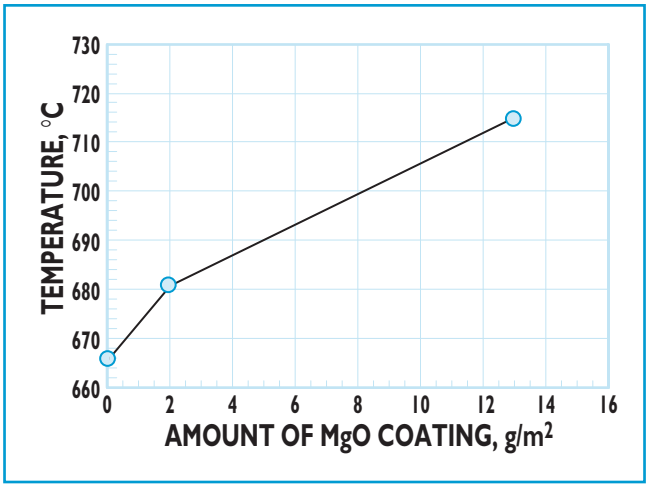
Figure 2 shows the dilution effect of a hypothetical, solid, nonreactive additive on the sticky temperature of superheater deposits as a function of chloride content. The sticky temperature is the temperature at which the deposit contains 20% molten phase. For a typical deposit that has a chloride content of about 1.5 mole percent Cl/(Na + K) even when the additive content is as high as 10% by weight, the sticky temperature can only increase by 7°C from 723°C to 730°C (1330°F to 1350°F). The effect is greater as the chloride content increases. Above 6.3 mole percent Cl/(Na + K), the effect decreases and eventually becomes zero because of the dramatic increase in molten phase caused by high chloride content. If the additive content is smaller than 0.1% by weight as suggested by chemical analysis, the deposit sticky temperature can increase by less than 0.1°C at 1.5 mole percent Cl (Na + K) and by a maximum of 0.2°C at 6.3 mole percent Cl (Na + K).

These estimations clearly suggest that the amount of additive typically used in recovery boilers is too small to affect deposit sticky temperature. The dilution theory is therefore unlikely to be the mechanism by which additives work in recovery boilers.

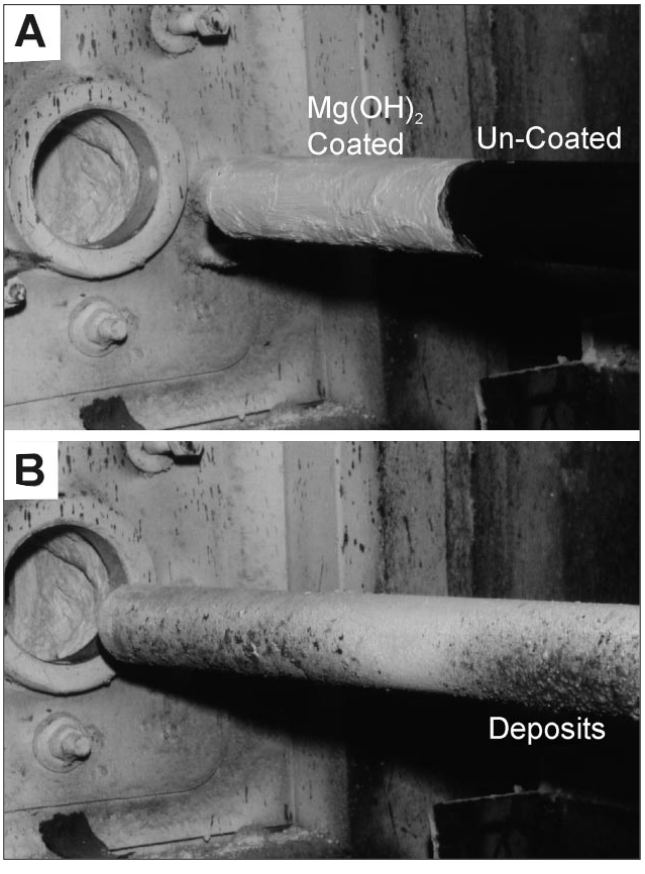
Combustion catalysis

This type of additive is available as liquid and solid. Liquid additives contain manganese, other proprietary compounds, or both. Solid additives usually contain MnO, MnO_2, or both as active components. If the active ingredient, Mn, serves as a combustion catalyst to help ensure the complete combustion of the black liquor, it can minimize the concentration of reduced sulfur compounds (primarily Na_2S) in carryover particles or deposits. Oxidation of Na_2S increases the deposit melting temperature to make the deposit less sticky. While the claim is plausible in principle, it is unlikely to work in practice for the following reasons:

- The strong reducing condition in the lower furnace and the short residence time of carryover particles make function of the additive as a combustion catalyst impractical.
- The minimum melting temperature of the Na_2S-Na_2SO_4-Na_2CO_3 system is about 740°C (1360°F). Below this temperature, the effect of Na_2S on deposit sticky temperature is insignificant compared with that of chloride and potassium *(8)*. Even if all reduced sulfur compounds could be oxidized, the effect on the deposit sticky temperature would be minimal particularly in the region from the middle superheater section onward. The flue gas temperature here is usually lower than 740°C.
- The amount of Na_2S in carryover deposits in the superheater region is typically small at <2% by weight for boilers without additives *(9)*. The effect of a combustion catalyst additive on deposit thermal properties is likely to be very small.
- Carryover deposits usually contain a small amount of "native" Mn that comes primarily from wood. The concentration of Mn in deposits and precipitator dust in boilers using Mn containing additives is the same as or slightly higher than when not using the additive. Even if the additive works, concluding whether the effect is due to the "added" Mn or the "native" Mn is therefore difficult.
- If reduction of the Na_2S content is the primary working mechanism, such additives should not affect fume deposition since fume deposits contain no reduced sulfur compounds.



3. Effect of MgO coating on sticky temperature of a synthetic deposit



4. Air cooled probe coated with $Mg(OH)_2$ (a) before the test and (b) after exposing at the boiler bank inlet for 1.5 h

Cleavage plane formation

This type of additive consists of essentially the same materials as the dilution type. The difference is that it works by a different mechanism. When high melting point oxides such as MgO, CaO, and MnO are applied directly on the tube or deposit surface, they form a loosely bonded layer or "cleavage plane" between the substrate and subsequently formed deposits *(3, 4)*. The cleavage plane prevents new deposits from adhering tenaciously to the substrate surface, makes deposits stratified and friable, or both. This eases their removal by sootblowers.

The mechanism is technically sound since it requires a smaller amount of material to form an effective cleavage plane within a deposit body than to "dilute" an entire deposit effectively. The validity of this mechanism has been confirmed in the laboratory *(10)*. As **Fig. 3** shows by coating a metal substrate surface with a layer of MgO powder, the sticky temperature of a synthetic deposit pellet—defined by the onset of strong adhesion—can increase by 30°C–70°C depending on the amount of coating.

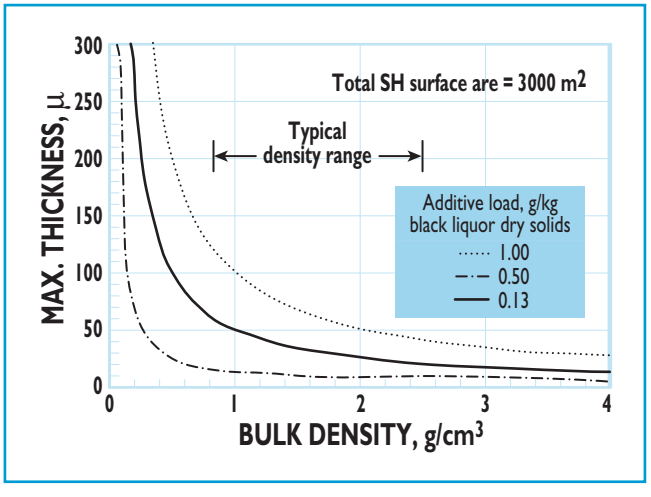
A field study using an air-cooled probe also showed this positive effect of MgO. A section of the hot end of the probe was painted with a water slurry of MgO and dried to form the 1 mm thick $Mg(OH)_2$ coating of **Fig. 4 a**. The probe was inserted into a recovery boiler through an opening near the boiler bank inlet where the flue gas temperature was about 670°C (1240°F). At this temperature, $Mg(OH)_2$ must have decomposed quickly to form MgO because of its low decomposition temperature of about 350°C (660°F). After exposing the probe for 1.5 h, the windward side of the MgO coated section of the probe was covered with a thin layer of 1–1.5 mm of deposit. On the uncoated probe surface, a thick, dense deposit was observed as Fig. 4 b shows. Clear evidence existed during the test that sootblowers blew off some deposits. For tests in which only a thin $Mg(OH)_2$ coating of <0.2 mm was applied, no significant difference was observable between deposits on the coated and uncoated sections of the probe. For tests in which the probe had no MgO coating, the deposition pattern was the opposite of that in Fig. 4 b. It had a thick layer of carryover deposits at the hot end and a thin layer at the cold end.

These studies indicate that MgO or $Mg(OH)_2$ can be effective in controlling deposit accumulation in recovery boilers. A large quantity is necessary, and delivery to the tube surface must be effective. This is not easy in an actual boiler because of the physical constraint of the additive treatment and the limited quantity of additive used. The cleavage plane may not be sufficiently thick to provide a positive result.

Examination of the thickness of a hypothetical cleavage plane that an additive might form is interesting. One can estimate the maximum thickness assuming the

Sampling location	Sample color	Mg, ppm	First melting temperature °C
Superheater near screen tubes	White	51	576
	Grey	19	571
	Pink	1	n/a
Superheater near generating bank	White	45	575
	Grey	5	572
	Mixed (More pink)	11	n/a
Dust from boiler bank ash hopper	Mixed (More grey)	15	n/a

I. Mg content and first melting temperature of depositsamples from a recovery boiler under a MgO additive treatment



5. Maximum thickness of a hypothetical cleavage plane formed on the superheater tube surface in an ideal case as a function of additive load and bulk density

following "ideal" conditions:

- The additive is injected uniformly into the boiler in the superheater region
- The superheater tube surface is perfectly smooth
- No mixing occurs between the additive and the deposit
- Additive material all goes to the coating layer (cleavage plane) on the tube surface (None follows the flue gas stream to a location beyond the superheater.).

Consider a case in which the recovery boiler burns 75,000 kg/h (4 million lb/day) of black liquor dry solids and has a total superheater surface area of about 3,000 m^2 (32,000 ft^2). The additive is injected continuously for 4 h at a mass flow rate of 10 kg/h or 0.13 g/kg of black liquor dry solids. The total additive mass consumed over that time is 30 kg. This mass would have a volume of 16,000–50,000 cm^3 depending on the additive bulk density. This is typically 0.8–––2.5 g/cm3.

Figure 5 shows the calculated maximum thickness of a hypothetical cleavage plane formed on the superheater tube surface in an ideal case as a function of additive load and bulk density. For a typical additive load of 0.13 g/kg of black liquor dry solids, the maximum cleavage plane thickness would range from 5 µm with a bulk density of 2.5 g/cm^3 to 17 µm for a lower density additive of 0.8 g/cm^3.

In reality, the cleavage plane thus formed should be much thinner (perhaps 10–100 times) for the following reasons:

- Due to the small particle size of <1 mm and the non-sticky nature of the additive, much additive material would not deposit on the superheater tube surface. It would follow the flue gas to the back side of the boiler where it would collect in the electrostatic precipitators.
- The additive is usually injected continuously into the boiler at a small rate vs. a one time, large dosage injection. It spreads and mixes with the deposit more than remaining together to form a uniform, single compound cleavage plane.
- Since the tube surface is covered with deposits, it is no longer smooth. To obtain the same coating thickness, more additive material is necessary to cover the rough surface than the smooth surface.

Table I summarizes the results of chemical and thermal analyses of deposits collected at various locations in a boiler treated with a MgO additive. At each location, deposits appear stratified with white (probably fume), pink (carryover), and grey (mixture of fume and carryover) layers. In all samples, the Mg concentration was <51 ppm or less than 0.01% by weight if expressed as MgO. The white layer consistently contained more Mg than the pink and grey layers. No significant difference in the deposit first melting temperature was observable.

These results suggest that most additive follows the flue gas stream for collection in the precipitator. The supposedly formed cleavage plane if it exists must also be very thin or mixed with deposits. Such a thin, discontinuous cleavage plane is probably not effective in controlling deposit accumulation. While technically sound, the cleavage plane formation theory is therefore probably not the mechanism by which additives work in recovery boilers.

Note from Fig. 5 that the cleavage plane thickness increases dramatically as the additive bulk density decreases below 1 g/cm^2. The cleavage plane mechanism may prevail if using a large quantity of very low density additive.

Others

Titanium oxide use has given no conclusive results. It supposedly works by converting Na_2S in the deposit into "refractory" titanium sulfides to make the deposit less sticky. As with the combustion catalyst additives, this claim cannot be true because it relies on Na_2S, a minor component in the deposit, to be a target for the additive.

Note that the TiO_2 may adversely influence deposit removal since it reacts readily with molten Na_2CO_3 to form sodium titanate, $Na_2O{\cdot}TiO_2$. This is a common reaction in an autocausticizing process *(11)*. Spraying TiO_2 into a boiler at an elevation above the tertiary air ports may cause hard deposits to form in the superheater region. This is the result of $Na_2O{\cdot}TiO_2$ formation that acts to bind the deposits together.

Vermiculite, a hydrated magnesium-aluminum-iron-silicate mineral, has also been proposed as an additive. This mineral has a peculiar thermal property. It expands rapidly at temperatures above 650°C (1200°F) to a volume 15–20 times larger than its original volume. If mixed with deposits in the boiler, vermiculite might expand like "popcorn" to reduce drastically the deposit strength and make the deposit more friable and easier to remove. Vermiculite is effective in controlling fouling in coal-fired boilers, although no knowledge of its use in recovery boilers is available. The concept is interesting nevertheless.

SIDE EFFECTS CAUSED BY ADDITIVES

If introduced into the boiler with black liquor, additives will become part of the smelt. If injected with air in the upper furnace, additives will become part of the precipitator dust collected and fed back to the black liquor or part of the deposits in the upper furnace. These are removed by sootblowers, fall into the furnace heart, and ultimately become part of the smelt. Despite how additives are applied, they will therefore eventually enter the smelt and the chemical recovery cycle via the dissolving tank.

Nonprocess elements introduced via an additive into the chemical recovery cycle may or may not cause a side effect depending on whether they can accumulate in the liquor system. The degree of accumulation depends strongly on the solubility in green and white liquors, compounds derived from the additive, settling rate of the precipitates with the dregs, and separation efficiency of slakers and green/white clarifiers.

Examining how compounds of the major elements in additives, i.e., Si, Al, Ca, Mg, Mn, and Fe, react with smelt, green liquor, and white liquor is important as are the side effects they may cause in the recovery cycle.

Silicon

Silicon in the additive primarily has the form of silica (SiO_2), the main component of sand, clay, and other silicates. Depending on the particle size of the additive and the smelt temperature, SiO_2 may react readily with Na_2CO_3 to form sodium silicates ($nNa_2{\cdot}SiO_2$) but not with Na_2S. In the dissolving tank, sodium silicates dissolve to release free SiO_3^{2-} into the solution. Unreacted SiO_2 remains as suspended solids, although a small portion of it may dissolve in green and white liquors due to the high pH of the liquors. In slakers and causticizers, some dissolved SiO_3^{2-} ions react with $Ca(OH)_2$ to form calcium silicate hydrate (CSH) gels. The gels do not settle readily in clarifiers and therefore do not remove completely from the system with dregs and grits. As a result, Si accumulates in the liquors.

Potential problems associated with the use of additives containing SiO_2 include increased smelt viscosity that may hinder the smelt flow, slow mud settling rates, blocking of mud filters by CSH gels, increased tendency for the production of dead-burned lime, poor product lime availability and causticizing efficiency, and severe scaling in evaporators.

Aluminum

Aluminum in additives is as alumina (Al_2O_3), clay, or other aluminosilicates. Although Al_2O_3 is generally not as reactive as SiO_2, it also reacts with Na_2CO_3 to form sodium aluminate ($NaAlO_2$) and does not react with Na_2S.

In the dissolving tank, $NaAlO_2$ hydrolyzes to form NaOH and water insoluble aluminum hydroxide, $Al(OH)_3$, aluminum oxide hydrate ($Al2O_3{\cdot}nH_2O$), or both. Since the hydrolysis reaction is slow and the precipitated $Al(OH)_3$ and $Al_2O_3{\cdot}H_2O$ may be in a gel form that does not settle readily, removing Al compounds from the liquor system through dregs and grits may be difficult.

A high Al concentration in the liquors may result in severe scaling in black liquor evaporators *(12)*. In lime kilns, the effect of high Al_2O_3 on lime quality should be insignificant since Al_2O_3 does not react with CaO at temperatures prevailing in the kiln. If Al originates from clay or other aluminosilicates in the additive, it will be present in the liquors, suspended solids, and lime mud with Si. Al may then aggravate problems caused by Si.

Calcium

If the calcium in the additive is as calcium silicates, it will form sodium calcium silicates with Na_2CO_3 in the smelt. If it is in the form of CaO or $Ca(OH)_2$, it will remain as or become CaO. CaO does not react with molten Na_2CO_3 but may react with Na_2S to

form CaS in the presence of CO_2 according to the following:

$$CaO(s) + Na_2S(l) + CO_2(g) \rightarrow CaS(s) + Na_2CO_3(l)$$

In the dissolving tank, CaO reacts with water to form $Ca(OH)_2$ that subsequently reacts with Na_2CO_3 to form NaOH and $CaCO_3$. The precipitated $CaCO_3$ is likely removed with dregs or becomes part of the lime mud.

Since the amount of Ca originating from an additive is much smaller than that from lime, the added Ca is unlikely to cause an additional side effect. One negative effect of CaO and $Ca(OH)_2$ when used as an additive is the possible formation of hard, difficult to remove $CaSO_4$ deposits in the back side of the generating bank and in the economizer.

Magnesium

Magnesium generally behaves in the same way as calcium. If it enters the smelt as magnesium silicates, it may be dissolved in the smelt by reactions between the silicates and Na_2CO_3. If it comes in as MgO or $Mg(OH)_2$, it would be present as MgO in the smelt. At temperatures prevailing in the lower furnace, MgO does not react with Na_2CO_3 or Na_2S.

In the dissolving tank, most MgO reacts with water to form $Mg(OH)_2$, and some may become $MgCO_3$. These compounds are extremely insoluble particularly in a strongly alkaline solution such as green or white liquors. They precipitate readily and can be removed from the liquor system with dregs and grits. Magnesium is therefore unlikely to accumulate and cause problems in the recovery cycle.

Manganese, titanium, and iron

Oxides of these elements react with molten Na_2CO_3 to form sodium manganate, titanate, and ferrite. They also react readily with Na_2S in the smelt to form sulfides (MnS, TiS_2, and FeS) in the presence of CO_2 in the lower furnace as follows:

$$MnO(s) + Na_2S(l) + CO_2(g) \rightarrow MnS(s) + Na_2CO_3(l)$$

These sulfides are very insoluble in water and may be removed from the system with dregs. Using additives containing these elements inevitably results in the depletion of sulfides in the liquor. A sulfur makeup is necessary.

In summary, MgO and $Mg(OH)_2$ seem the best of all commonly used additives, since they do not react with Na_2CO_3 and Na_2S in the smelt and are unlikely to accumulate and cause problems in the recovery cycle. The second best additives are CaO and $Ca(OH)_2$.

CONCLUSIONS

Various fireside additives have use to control deposit accumulation in recovery boilers. The results have not been conclusive primarily due to the high content of "ash" in the black liquor and the high alkali content of the deposits.

Of the three currently most cited mechanisms (dilution, combustion catalysis, and cleavage plane formation), cleavage plane formation may be the most logical since it requires the least amount of additive material. Even this mechanism cannot satisfactorily explain how a small quantity of additive can be effective in recovery boilers.

This does not mean that additives do not work at all in recovery boilers. The positive results recently experienced with the injection of a small amount of $Mg(OH)_2$ into the superheater region indicate that the additive may work perhaps for an undetermined reason. One possible explanation is that $Mg(OH)_2$ may be highly porous and have a high specific surface area depending on its source. When injected into the boiler, it decomposes into an even more porous MgO. Such a porous material may act like a "sponge" absorbing the molten phase from the deposit through a capillary action. This makes the deposit "dryer" and less sticky.

This sponge mechanism and perhaps the cleavage plane formation mechanism require further examination in the laboratory before drawing any definite conclusion on the effectiveness of additives. The potential material for the sponge mechanism to work may be MgO, $Mg(OH)_2$, or any other high melting temperature compound with a low density and high porosity. It must also not react with smelt and be readily separated and removed from the liquors with dregs and grits.

Additives should have little impact on fume deposition in the generating bank and economizer because of the large quantity of fume and the low gas temperature in these regions. Sometimes, additives used in recovery boilers must compete with fume deposits for their effectiveness. Note that fluffy, powdery fume deposits that always form on the surface of screen tubes, low-temperature superheater tubes, and boiler bank tubes can serve as an excellent coating material to weaken the bond between the tube and carryover deposits. The cleavage plane formed by fume deposits can be 1–2 mm thick and can help deposit removal by sootblowers.

Although most additives do not affect deposit properties, they also cause no harm because of the low dosage. Depending on the material used, additives may cause serious problems in the recovery cycle if applied in large quantities. Si and Al based additives may cause severe scaling in evaporators, slow mud settling rates, blocking of mud filters in the causticizing plant, poor lime quality, and refractory damage in lime kilns. Additives containing Mn, Ti, Fe, or other transition elements may result in sulfur losses. Among the commonly used additives, MgO, $Mg(OH)_2$, CaO, and $Ca(OH)_2$ seem best. They cause the least side effects. **TJ**

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