The Growth of Dry Sorbent Injection (DSI) and the impact on Coal Combustion Residue

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INTRODUCTION

Dry Sorbent Injection (DSI) refers to the practice of injecting a dry alkaline mineral into a flue gas stream in an effort to capture acid gases. The use of this technology at utilities and industries is expanding rapidly as a low capital cost solution for compliance with evolving environmental control requirements. This paper discusses the drivers for the use of DSI technology and the potential impacts of the DSI reagents on the Coal Combustion Residue (CCR), whether disposed or marketed.

THE DRIVERS FOR DRY SORBENT INJECTION (DSI)

DSI technology was evaluated as a potential acid gas control technology as early as the 1980’s, however as a general rule, capture efficiencies were not high enough to address the removals required at utility coal-fired boilers under Phase One SO_2 control requirements of the 1990 Clean Air Act Amendments. However, advances in sorbent effectiveness, combined with new regulatory drivers, have DSI playing a major role in U.S. utility and industry compliance strategies.

Much of the recent rebirth of DSI technology was driven by the unintended consequence of installing SCR technology on coal-fired utility boilers combusting high sulfur fuel. Unfortunately retrofitted SCR systems designed to capture NO_x also convert some percentage of SO_2 to SO_3. This SO_3 has become a major issue for many utilities as the SO_3 reacts with moisture in the flue gas and atmosphere as the gas cools. This has resulted in localized H_2SO_4 emissions or so called “blue plume” issues. Over the last ten years, DSI with both calcium and sodium products have proven effective for control of SO_3 emissions and are in use at dozens of facilities today.

Three additional rule making efforts aimed at coal-fired utilities are expanding the interest in DSI technology. Perhaps most significant is the implementation of the utility MATS rule, which requires control of HCl emissions from coal-fired power plants for the first time. In fact, the U.S. EPA has estimated that 62 GW of coal-fired utilities will utilize DSI technology to comply with the recently finalized utility MATS rule. While the validity of this estimate is certainly debatable, the use of DSI technology at coal-fired plants is clearly growing.

Also impacting the interest in DSI technology is the reemergence of the regional haze rule making efforts and reimplementation of CAIR as a result of the vacature of the Cross State Air Pollution Rule (CSAPR). All of these rules will require coal-fired units that do not have acid gas scrubbers installed to evaluate their options for controlling acid gases including SO_2, HCl and higher levels of SO_3. It is also clear that controlling these acid gases will require utilization of much higher amounts of DSI reagent than that already experienced for basic SO_3 control. It is these higher levels of DSI reagents that have the potential to dramatically impact the properties of the CCR from a given facility.

BASIC CHEMISTRY OF DSI REAGENTS

The chemistry associated with DSI technology is relatively straight forward and well understood at this point. The two primary chemistries being utilized for utility acid gas control with DSI are calcium based and sodium based. The primary calcium reagent being widely utilized is hydrated lime or calcium hydroxide ($Ca(OH)_2$) and the basic reactions that result in the capture of SO_2 and HCl are outlined below.

$$\mathbf{Ca(OH)_2 + SO_2 + .5O_2 \longrightarrow CaSO_4 + H_2O}$$

$$\mathbf{Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O}$$

Accordingly, the primary reaction products of calcium based DSI are calcium sulfate and calcium chloride. Given the relative volume of sulfur compounds vs. the lower concentration of chlorides in a typical flue gas stream there is generally quite a bit more of the sulfate reaction products than chloride reaction products present. Note that there are other less critical reaction products resulting from interaction with Hydroflouric acid and even CO_2 in the flue gas, but the primary reaction products are those associated with sulfates and chlorides.

The sodium based chemistry is a bit more complex in that both trona (sodium sesquicarbonate) and sodium bicarbonate can be used in sodium based DSI applications. However, the reaction products are ultimately the same for either compound. The basic trona reaction for sulfate capture is outlined below[1].

$$\mathbf{2(Na_2CO_3 . NaHCO_3 . H_2O) + 3SO_2 \longrightarrow 3Na_2SO_3 + 4CO_2 + 5H_2O}$$

Secondary sulfate capture reaction is as follows:

$$\mathbf{3Na_2SO_3 + 1.5O_2 \longrightarrow 3Na_2SO_4}$$

The basic chloride capture mechanism for sodium reagents is as follows [1]:

$$\mathbf{Na_2CO_3 . NaHCO_3 . H_2O + 3HCl \longrightarrow 3NaCl + 2CO_2 + 4H_2O}$$

In the case of the sodium chemistry the primary reaction products are sodium sulfate and sodium chloride. Just as with calcium, there is generally much more of the sulfate reaction product than the chloride reaction product due to the relative concentration of the pollutants in a coal-fired utility typical fuel gas.

FACTORS THAT IMPACT DSI SYSTEM EFFECTIVENESS

DSI is being employed for a wide variety of acid gas control applications. At unscrubbed utilities, DSI technology is being employed for primary SO_2 control as well as a viable approach for HCl compliance for the MATS rule. At scrubbed utility units, DSI technology is generally employed for SO_3 control. However, there is a growing population of facilities using DSI technology to remove chlorides from the scrubber chemistry and minimize the use of activated carbon for mercury control. Regardless of the specific application, the effectiveness of a DSI system is a function of the three broad categories of factors listed below:

- Flue Gas Properties –Temperature, flue gas moisture and other competing acid gases (SO_3, HCl, HF and SO_2)
- Reagent Properties – inherent reagent reactivity, reagent surface area, reagent porosity, pore geometry
- Injection System Configuration - Particulate control device, in flight residence time, reagent mixing and injection location

In addition to impacting the effectiveness of a DSI system for a given control requirement, the impacts of a DSI system on the CCRs are influenced by these factors as well. While the use of DSI reagents at utilities using wet scrubbers for SO_2 compliance will clearly impact the scrubber sludge, this presentation will focus primarily on the impacts to the fly ash, whether marketed or disposed.

INJECTION SYSTEM CONFIGURATION IMPACTS

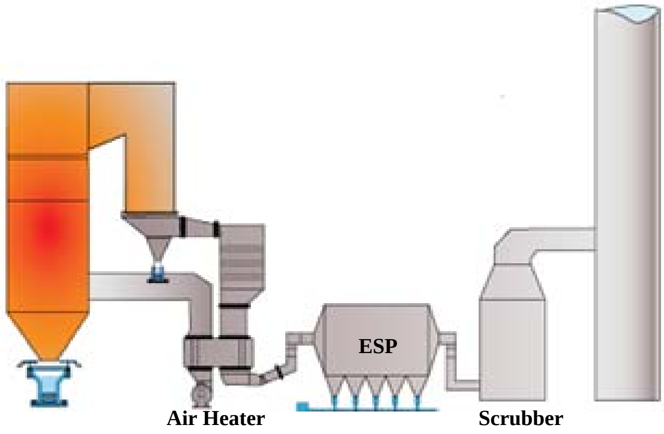


Figure One

Clearly the selection of where a DSI reagent is introduced will have differing impacts on the CCR materials. The current trend on employing DSI systems is to move the system further back towards the boiler in an effort to gain the benefits of removing the acid gases earlier in the post combustion control system. The major benefits that are being realized from this approach are related to 1) removing SO_3 prior to the air heater, thereby reducing the potential for ammonia bisulfate formation in the air heater and 2) removing the SO_3 in advance of activated carbon injection (ACI) to improve the performance of the carbon for mercury capture. However, an injection of a DSI reagent prior to the particulate control system will inevitably result in impacts on the CCRs.

If maintaining the marketability of a fly ash stream is a priority for a given plant, it may be possible to install a DSI system allowing for injection of the reagent immediately after the existing particulate collection system. However, while this approach will mitigate impacts on the fly ash, there are significant trade-offs. The first issue is that if the existing wet FGD system can not handle the additional particulate loading associated with the DSI reaction products, a secondary particulate collection device dedicated to the capture of the DSI reaction products would have to be retrofitted.

Alternatively, the wet FGD system may be capable of handling the additional particulate loading resulting from the DSI reagent. In this instance, the use of $Ca(OH)_2$ results in sulfate reaction products that are the same as those for the FGD scrubber itself, namely $CaSO_4$. Use of sodium based reagents would result in sulfate reaction products that are inconsistent with the marketing of the FGD process synthetic gypsum and therefore require additional processing or disposal of the scrubber sludge.

An additional issue with the approach of injecting post existing particulate collection system, and relying on the FGD system for DSI reaction product capture, is that the reagent will be less effective due to reduced residence time. This would result in higher reagent consumption for a given level of acid gas control.

REAGENT REACTIVITY CONSIDERATIONS

Regardless of how the DSI system is configured, the reactivity of the DSI reagent will determine how significant an impact a DSI reagent will have on the fly ash stream. As an example, if a higher reactivity sorbent (whether sodium or calcium) is used, less unreacted sorbent will be present in the CCR stream.

In the case of a calcium sorbents, the reactivity of a reagent is primarily a function of the calcium hydroxide surface area, pore volume and pore geometry. This means that a calcium hydroxide optimized for acid gas capture will require less reagent for a given level of control and therefore would result in less unreacted $Ca(OH)_2$ in the residue.

The reactivity of sodium based DSI sorbents is a function of the form of sodium, sodium bicarbonate or sodium sesquicarbonate (trona) as well as particle size. Trona is commonly milled prior to use in DSI systems in an effort to improve its reactivity for acid gas applications. The choice of sodium reagent and pre-injection treatment will impact the amount of residual sodium bicarbonate or sodium sesquicarbonate in the CCR.

FLUE GAS PROPERTIES

The flue gas properties at the injection point will impact how reactive a DSI reagent is with specific acid gases. This in turn will impact how much the CCR will be impacted. As an example, while optimized calcium hydroxide is quite reactive with SO_2 at higher temperatures, at lower injection temperatures such as those typically encountered post air heater, hydrated lime not very reactive with SO_2. This would suggest that if the goal of a DSI system is to capture HCl for MATS compliance and minimize the impact on the CCR residue, injection of hydrated lime at post air heater temperatures would be preferred.

Conversely, since sodium compounds are relatively reactive with SO_2 regardless of temperature, a significant amount of SO_2 would be captured even when targeting HCl. This would result in an increase in the sulfate reaction compound, sodium sulfate (Na_2SO_4) in the CCR material.

It is clear that the DSI injection system configuration, reagent properties and flue gas properties will determine the efficacy of the system and the resulting impacts on the CCRs. And while the impacts can be minimized to an extent, the questions of how the marketability of a fly ash stream and the potential liability associated with disposal of CCRs impacted by DSI reagents remains. The potential impacts of DSI reagents on the disposal of CCRs are addressed first.

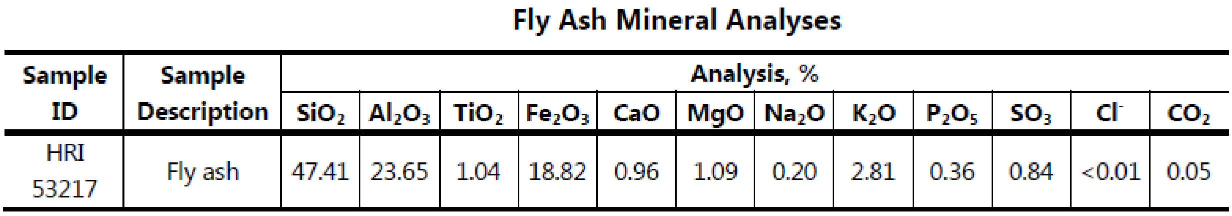
THE IMPLICATIONS OF THE USE OF DSI REAGENTS ON DISPOSED CCRs

While maintaining the marketability of fly ash after the implementation of DSI technology is the desired outcome, it is likely that that a majority of fly ash impacted by DSI reagent use will be disposed. Given the focus of the EPA on developing rules for disposed CCRs, the impact of these DSI reagents must be considered.

While the most obvious impact will be an increase in the volume of CCR materials, the impacts that are likely more significant are the impacts on the metals leaching potential of the fly ash and the soluble constituents of the resulting fly ash. While it is recommended these impacts be evaluated for each specific fly ash, Lhoist North America (LNA) determined it would be useful to develop a method to evaluate the relative impacts of calcium hydroxide DSI reagents versus sodium based sorbents for these specific properties in a laboratory environment.

Bench Test Design

While we are aware of at least one unit switching from sodium DSI reagents to calcium DSI reagents, there was not any data available to compare the relative impacts on the associated CCR materials. Also, any changes in fuel or unit operations would present a significant challenge in analyzing any available data. Accordingly, LNA elected to enlist a third party laboratory to perform a series of bench scale tests on split samples of an actual bituminous coal fly ash in an effort to ascertain the relative impacts of using calcium DSI sorbents versus sodium sorbents. The mineral analysis of the raw ash used in this pilot testing is shown below.



Fly Ash Mineral Analyses

Sample ID	Sample Description	Analysis, %											
		SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	SO_3	Cl^-	CO_2
HRI 53217	Fly ash	47.41	23.65	1.04	18.82	0.96	1.09	0.20	2.81	0.36	0.84	<0.01	0.05

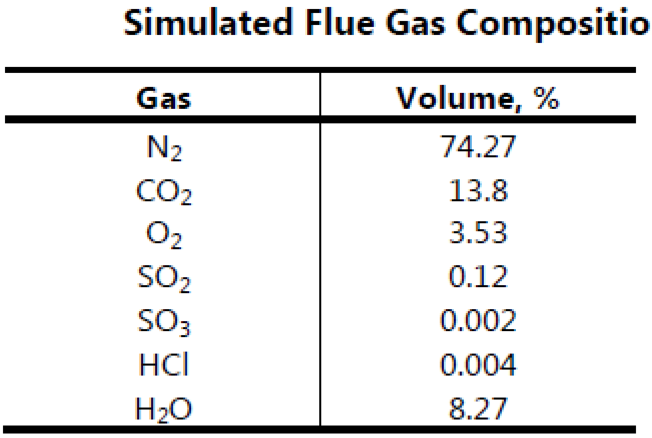
Table One

The bench scale test design then called for the fly ash to be blended with a percentage of DSI reagents and reacted with a typical coal fired flue gas stream in a batch kiln. Typical post combustion flue gas temperatures were used to drive the reaction between the DSI reagents with the acid gas pollutants in a manner consistent with the way this occurs in an actual dynamic DSI application. A photo of the batch kiln is shown below.

Figure Two: Batch Kiln System

In an effort to accurately predict the impacts of the use of DSI reagents on the CCRs, we then estimated the relative amount of DSI reagent necessary for two acid gas control requirements. When making these calculations we assumed the fuel was 1.2% sulfur, 0.1% chlorides, 10% ash and 10,000 Btu/lb. Typical stoichiometric rates for 90% SO_3 capture and 95% HCl capture were then assumed. These calculations resulted in two blends of DSI reagent by weight, one 15% DSI reagent and the second 30%, for both the sodium and calcium reagents. Note that even though the mass of DSI reagents are the same for both sodium and calcium, the difference in molecular weight between these two reagents (96 versus 56) means that a 70% higher stoichiometric rate is assumed for the given control level with the calcium reagent. This is likely a conservative assumption given that optimized hydrated limes have been demonstrated to compete very effectively with trona reagents on a weigh basis.

These blends were then subjected to a simulated flue gas consistent with the combustion of the typical bituminous fuel in a pulverized coal fired unit. Note that the temperature maintained in the batch kiln was 204° C or 399° F to represent post combustion conditions representative of those at typical DSI injection locations. The composition of the simulated flue gas is shown below.



Simulated Flue Gas Composition

Gas	Volume, %
N_2	74.27
CO_2	13.8
O_2	3.53
SO_2	0.12
SO_3	0.002
HCl	0.004
H_2O	8.27

Table Two

<u>Impact on metals leachability</u>

The raw fly ash, as well as the resulting combination of fly ash, DSI reaction product and unreacted reagent was then subjected to the SPLP leaching procedure per EPA method 1312. The leachates from these products were analyzed for heavy metals per EPA methods SW-846 6010C and SW-846-7470A with the results shown below.

SPLP Fly Ash and Fly Ash and Sorbent Mixture Analyses

Sample Description	SPLP Leachate Metals Assay,^{a} mg/L							
	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
SPLP Limits	5	100	1	5	5	0.2	1	5
Fly Ash	0.037	<1.0	<0.010	<0.010	<0.05	<0.0001	<0.05	<0.03
85% Fly Ash + 15% Na_2CO_3 (Solvair Select 200 Sorbent)	0.83	<1.0	<0.010	<0.010	<0.05	<0.0001	0.31	<0.03
70% Fly Ash + 30% Na_2CO_3 (Solvair Select 200 Sorbent)	3.3	<1.0	<0.010	0.027	<0.05	<0.0001	0.31	<0.03
85% Fly Ash + 15% $Ca(OH)_2$ (Sorbacal Sorbent)	<0.025	<1.0	<0.010	0.012	<0.05	<0.0001	0.07	<0.03
70% Fly Ash + 30% $Ca(OH)_2$ (Sorbacal Sorbent)	<0.13^b	<1.0	<0.010	<0.010	<0.05	<0.0001	<0.05	<0.03

EPA Methods SW-846 6010C and SW-846 7470A; leachate analyses provided by Accutest Laboratories (Wheat Ridge, Colorado).

Table 3

Note that for all samples, Barium, Cadmium, Lead, Mercury and Silver, results indicated metals leached at levels less then the detection limit. Chromium leached just above the detection limit of 0.010 mg/l with 15% calcium hydroxide and at 0.027 with 30% trona. The more interesting results are from Arsenic and Selenium, especially given that these are two of the primary metals of concern with fly ash CCR. The leaching results for both arsenic and selenium are represented graphically below.

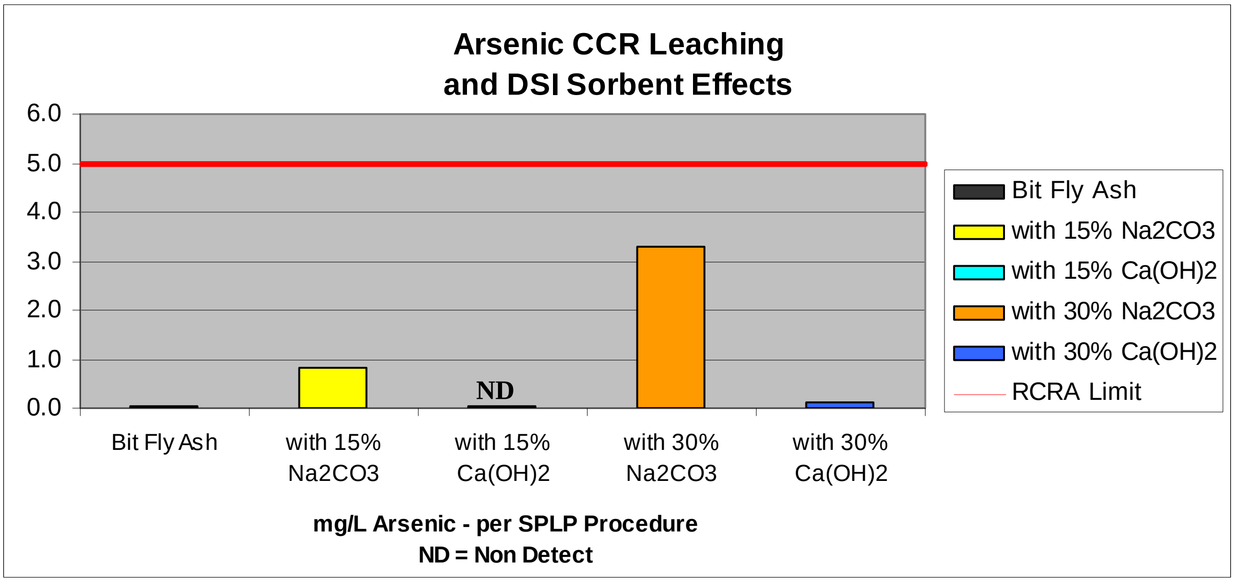


Figure 3

The data indicates a stark difference in the manner in which use of a sodium based reagent, trona in this case, impacts the leachability of arsenic for this fly ash. Conversely, while the addition of 30% calcium hydroxide results in measurable leachable arsenic, the amount of arsenic leaching from the sample associated with calcium based DSI reagent is 20 times less than the arsenic leaching from the sodium impacted material.

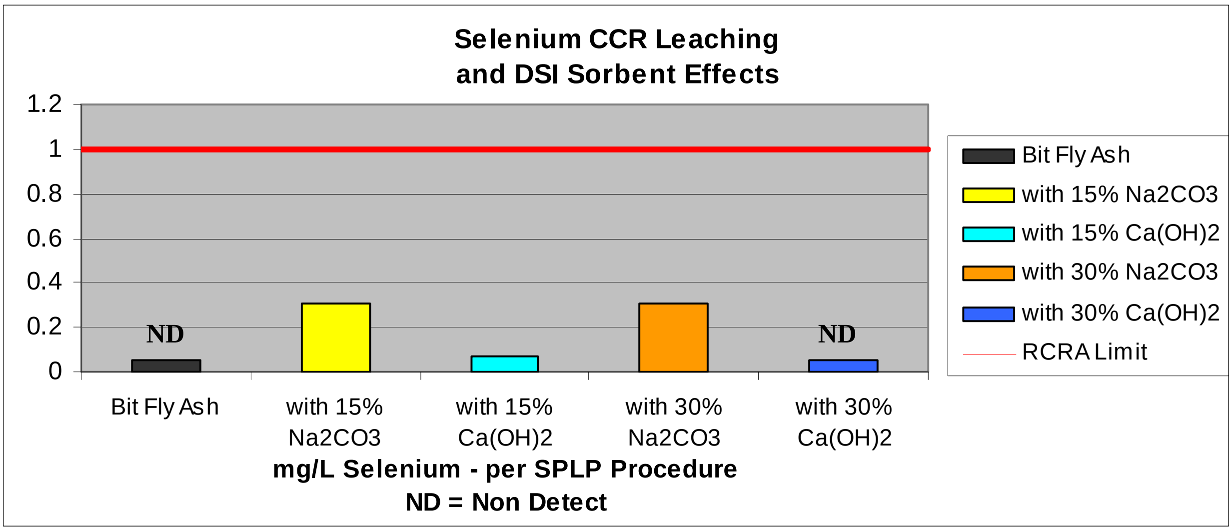


Figure 4

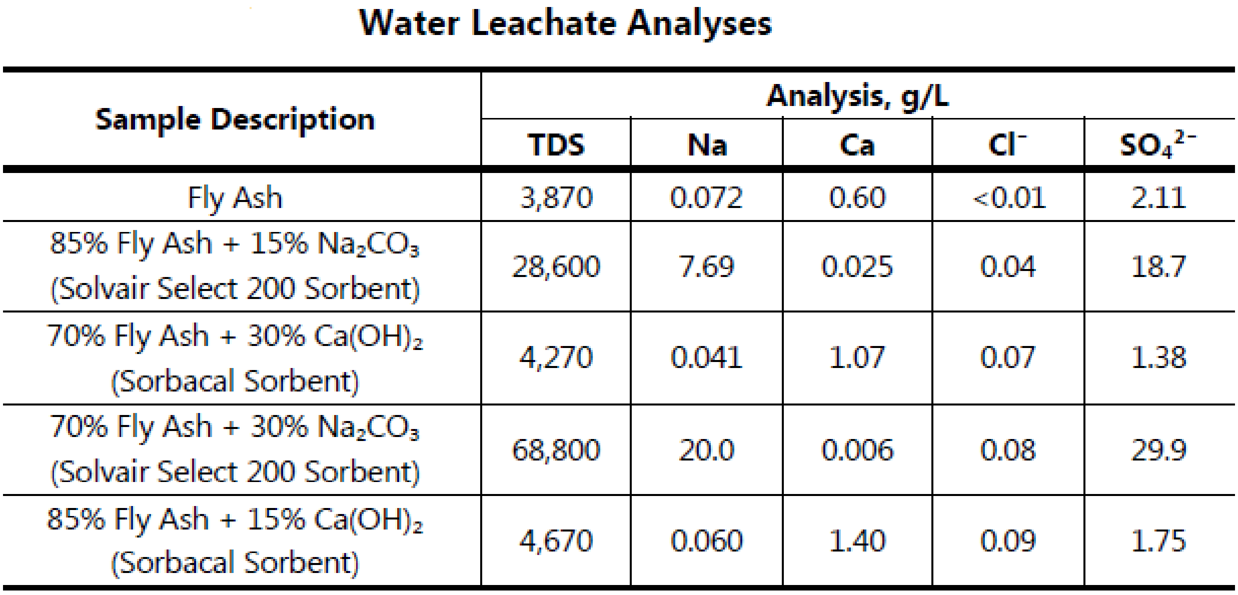
For selenium, the data indicates that again the fly ash subjected to treatment with a sodium based reagent results in a greater potential for leaching of this metal than that impacted by the use of a calcium hydroxide reagent. In fact, with 30% calcium addition, the resulting material leaches selenium at less than detection levels, just as the raw ash does.

While discerning the specific mechanisms at work here is beyond the scope of this bench testing, the results above are rational given the nature of the fly ash materials. Fly ashes are pozzolans, which by definition are finely divided siliceous compounds that react with water and calcium hydroxide to form compounds that exhibit cementious properties. Accordingly, it is likely that when calcium hydroxide is used as a DSI reagent some of the reagent that does not react with acid gases in the flue gas stream reacts with the pozzolan in the flue gas stream resulting in some metals being encapsulated in the process. There is an additional mechanism that will impact the metals leachability from a given fly ash. Since metals leachability is function of pH, the addition of alkaline DSI reagents will clearly impact the metal mobility for a given material. It is likely that this pH impact without any offsetting impacts from metal encapsulation is the reason the fly ashes impacted by sodium reagents exhibit elevated levels of metal leachability. It should be noted that this affect of pH impact will be different for every fly ash and accordingly, it is recommended that a site specific evaluation be performed to determine the impact of DSI reagents on metals leachability for a given CCR material.

Impact on Total Dissolved Solids

In addition to measuring the impact of the DSI reagents on metal leaching potential, the impact on the amount of soluble constituents that could be leached from a given fly ash were analyzed.

In an effort to determine these impacts, the roasted samples, as well as the raw ash were subjected to a deionized water leach. DI water was added to each sample until a 15% solids density was achieved. The sample was then agitated for 24 hours and the resulting slurry was filtered using a Buchner funnel with Whatman filter paper with 8-11 micron pore size. The resulting filtrates were then analyzed for sodium, calcium, chlorides sulfates and total dissolved solids (TDS) content. This approach was designed to evaluate relative leaching potential and not necessarily to model actual field leaching potential. These results are shown below.



Water Leachate Analyses

Sample Description	Analysis, g/L				
	TDS	Na	Ca	Cl^-	SO_4^{2-}
Fly Ash	3,870	0.072	0.60	<0.01	2.11
85% Fly Ash + 15% Na_2CO_3 (Solvair Select 200 Sorbent)	28,600	7.69	0.025	0.04	18.7
70% Fly Ash + 30% $Ca(OH)_2$ (Sorbacal Sorbent)	4,270	0.041	1.07	0.07	1.38
70% Fly Ash + 30% Na_2CO_3 (Solvair Select 200 Sorbent)	68,800	20.0	0.006	0.08	29.9
85% Fly Ash + 15% $Ca(OH)_2$ (Sorbacal Sorbent)	4,670	0.060	1.40	0.09	1.75

Table 4

In addition to the predictable differences in sodium and calcium compounds leaching form the reagents, there are dramatic differences in the leaching of both sulfates and total dissolved solids. The data above suggest that fly ashes impacted by sodium DSI reagents have ten fold the sulfate leaching of raw fly ash and of calcium impacted fly ash. In fact, the calcium impacted fly ash leaches sulfates at a lower level than the raw ash.

From a chlorides perspective both the sodium and calcium impacted fly ashes leached at higher levels than the non detectable levels of raw ash. While the amount of chlorides leaching from both impacted ashes was similar, the calcium impacted ashes tended to leach slightly higher amounts of chlorides than the sodium impacted ashes.

Again these results for both sodium and chlorides are predictable given the relative solubility of the reaction compounds. Below is a summary table of reaction product compounds as reflected in the CRC Handbook of Chemistry and Physics.

Reaction Compound	Cold H_2O Solubility*
N_2SO_4	**100**
$CaSO_4$	**0.21**
NaCl	**35.7**
$CaCl_2$	**74.5**

***Grams per 100 cc H_2O**

Table 5[3]

The impact on TDS is also quite significant. While both calcium impacted fly ashes indicate a 10-20% increase in total dissolved solids, the sodium impacted fly ashes reflect an order of magnitude difference in TDS leaching from both the 15% and 30% sodium fly ash blends. The dramatic difference in TDS between the calcium hydroxide (Sorbacal®) and sodium product (Solvair® Select 200) is illustrated below.

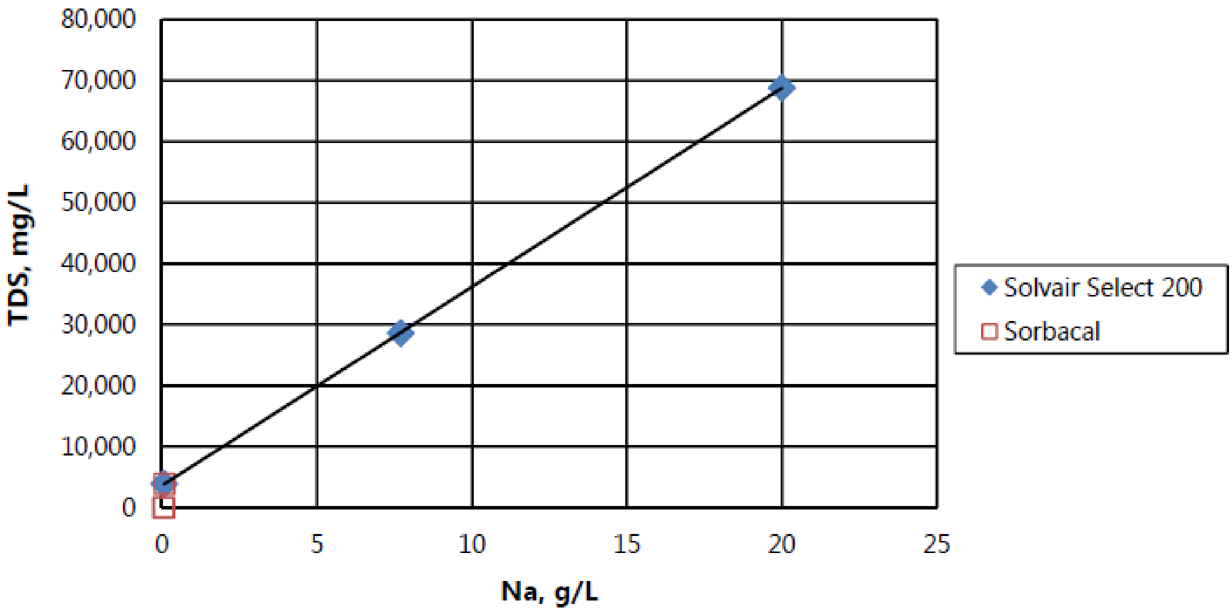


Figure 5

FLY ASH MARKETABILITY

The use of DSI reagents has both direct and indirect impacts on the marketability of fly ash CCRs. The direct impacts are a result of the acid gas capture reaction products and unreacted reagent being comingled with the fly ash. Whether these impacts will preclude marketing of the ash for concrete applications will be a function of the untreated ash characteristics and the amount of reagent required for a given acid gas application. However, it is possible to discuss some general impacts.

Direct Impacts

For some fly ashes an increase of unreacted $Ca(OH)_2$ and calcium reaction compounds, namely $CaSO_4$ and $CaCl_2$ will not necessarily preclude marketing of the ashes as these are compounds that are present in many fly ashes. However, at high DSI addition rates, these impacts could result in an ash that is problematic for use in ready mix applications due to the elevated calcium compounds.

For sodium based DSI reagents, the acid gas capture reaction compounds (N_2SO_4 and NaCl) and unreacted sodium reagent will contribute to available alkalis. Typically fly ashes to be used in ready mix applications are limited to 1.5% available alkalis. Most ashes already contain some level of available alkalis so the use of a relatively small amount of sodium DSI reagent may preclude marketing the resulting fly ash into ready mix applications. Again, this impact needs to be evaluated on a case by case basis for each fly ash.

Indirect Impacts

The most notable indirect impact of the use of DSI reagents for acid gas control is on the amount of Activated Carbon Injection (ACI) necessary to achieve mercury compliance for some fuels. While the ASTM limit on carbon for ash used in ready mix applications is 6%, the market limit is generally considered to be 3%. It is now generally accepted that SO_3 competes with mercury when reacting with activated carbon and therefore, reducing the amount of SO_3 present in a flue gas stream will improve the effectiveness of activated carbon. This is illustrated by the graph[4] below.

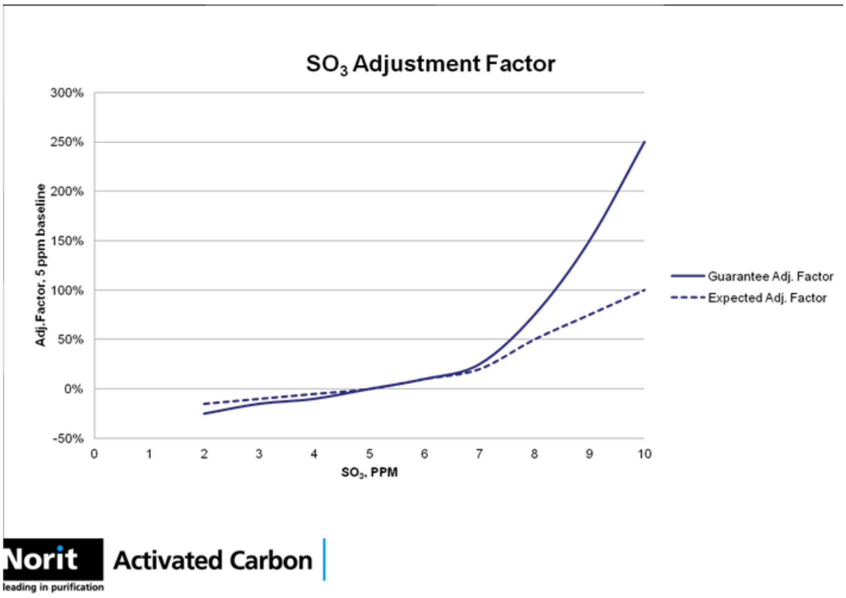


Figure 6

Accordingly, using a DSI reagent to minimize the amount of carbon necessary to achieve a given mercury control requirement can enhance the potential to continue marketing a fly ash impacted by the use of ACI. Note that while both calcium hydroxide and sodium sorbents have proven successful in the control of SO_3 over the last 10 years, recently a complicating factor has been identified when using sodium chemistry for acid gas control. This factor is the potential for sodium reagents to catalyze NO_x compounds to NO_2. Just as is the case with SO_3, NO_2 tends to compete for the activated carbon and can offset the benefits of SO_3 reduction. The potential for NO_2 generation is illustrated below in Figure 7 for a field trial performed by ADA Environmental Solutions. This data was presented at the recent Reinhold Environmental conference [5].

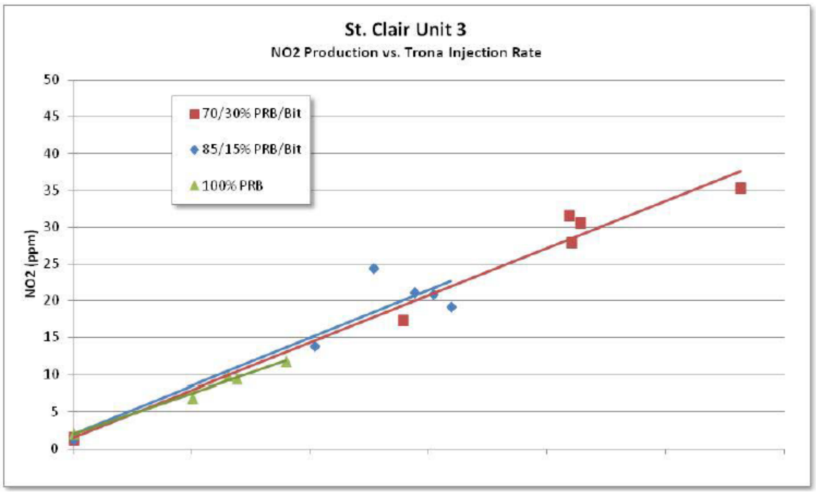


Figure 7

Figure 8 below illustrates the impact on the demand of activated carbon for a given mercury capture requirement as a function of the amount of trona utilized for acid gas capture.

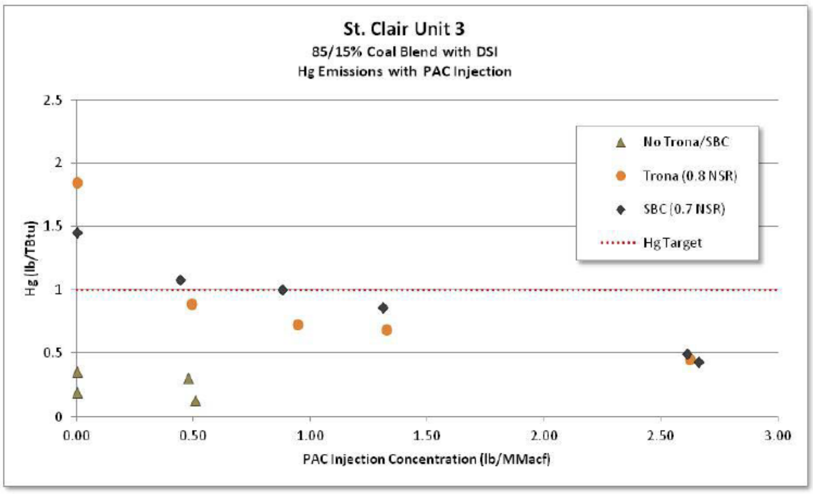


Figure 8

Note that despite the fact that the trona reagent almost certainly captured a significant percentage of the SO_3 present in the flue gas, the activated carbon consumption for a given mercury control requirement increased. This suggests that the effect of trona resulting in increased NO_2 in the flue gas stream more than offset the benefits of the SO_3 capture taking place. It is interesting to note that this appears to be the case even for the native mercury capture (at 0% activated carbon injection) meaning that the use of trona for acid gas capture could increase the mercury emissions for some systems.

SUMMARY

Evolving environmental control requirements being placed on coal-fired utilities and industries have spurred rapid development of Dry Sorbent Injection (DSI) technology for acid gas control requirements. While effective for controlling a wide variety of acid gases, the alkaline reagents utilized in DSI also impact the process coal combustion residue (CCR), especially the fly ash. Before selecting a given DSI reagent, the direct impacts on the CCR, whether marketed or disposed, must be considered. In addition, indirect impacts such as the resulting affect on activated carbon utilization for mercury control must also be considered.

REFERENCES

[1] Muziak, John, Solvay Chemicals, Successful Mitigation of SO_3 by Dry Sorbent Injection of Trona Upstream of the ESP, Presented at 2005 MegaSyposium

[2] "ASTM C618 – 12a Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete". ASTM International, Book of Standards, volume 04.02.

[3] CRC Handbook of Chemistry and Physics, 93rd Edition

[4] Nebergall, Rob, Norit Activated Carbon, Reinhold Environmental NO_x control conference, Panel discussion titled SCR Effects on Downstream Hg Control, February 18-19, 2013

[5] Sjostrom, Sharon, ADA Environmental Solutions, Mercury Control from Coal to Stack presentation, Reinhold Environmental NO_x control conference, February 18-19, 2013