One cloud at a time

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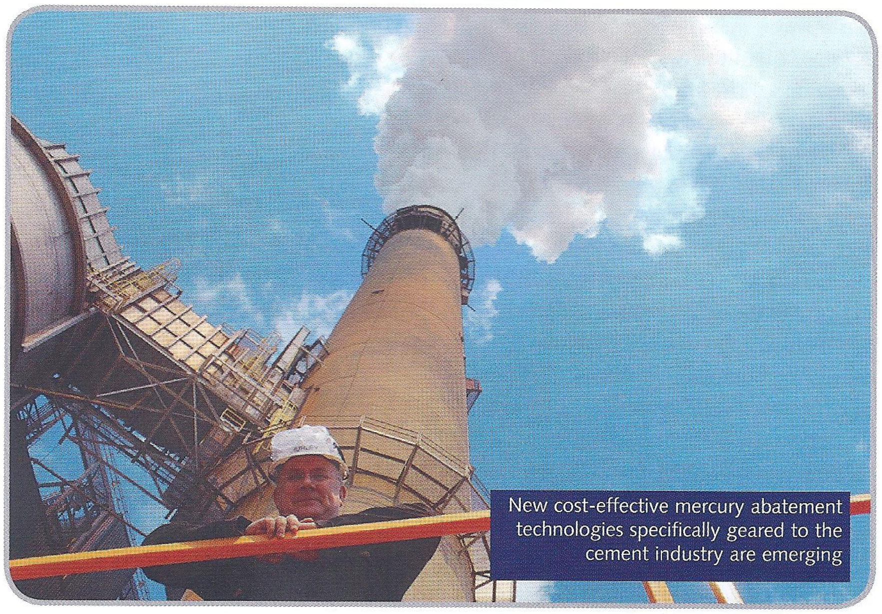
Heavy metals have long been recognised as hazardous to human health and none more so than mercury. Its status as a documented toxin is reflected by the recent adoption of the United Nations Environment Programme (UNEP) Minamata Convention. While mercury capture technologies are available, many were originally tailored for power sector application. However, new technologies geared specifically to the cement industry are now emerging.



New cost-effective mercury abatement technologies specifically geared to the cement industry are emerging

Mercury minerals are widespread through the earth's crust, with an average metal concentration of approximately 0.05mg/kg. If heated, these minerals would readily liberate mercury metal and/or its compounds. Estimated global mercury emissions from natural and anthropogenic sources range from 5000-8000t.[1,2,3] While Mother Nature contributes roughly two-thirds to half of these emissions – primarily from the oceans, volcanoes and geothermal vents – the balance of all discharges to the atmosphere are directly or indirectly attributable to human activity. Although estimates of natural emissions also encompass mercury re-emissions from historic anthropological discharges to the seas, mankind has been heating rocks of one form or another for millenia to change their chemical form, extract metals or release energy from fossil fuels. As a result, significant unwanted pollution has arisen with 2000t of current atmospheric emissions emanating from terrestrial anthropological sources.

UNEP's Minamata Convention obligates governments to control and "where feasible" reduce mercury emissions and mercury compounds to the atmosphere through measures to control emissions from point source categories such as coal-fired power stations, non-ferrous metal smelters, waste incinerators and cement kilns.

Mercury treatment options for cement kilns

To date national regulators have focussed their attention on the coal-fired power sector, which has historically contributed to around 25 per cent of terrestrial anthropological mercury discharges, with other atmospheric pollutants of concern (arsenic, nickel, chromium and selenium) being rolled up into the same regulations.

This regulatory pressure has driven a number of technology solutions for that sector. These solutions treat combustion gases with a variety of approaches as outlined below.

- **Dry mercury sorbents**
These include powdered activated carbon (PAC)/activated carbon injection (ACI) or amended silicates delivered into exhaust gas, with recovery of the spent sorbent by a baghouse fabric filter (FF) or electrostatic precipitators (ESP).

- **Wet mercury sorbents** – PAC dosed into wet flue gas desulphurisation (wet-FGD) scrubbers

- **Mercury oxidants**
These include calcium chloride or bromide applied to the fuel to generate hydrogen chloride (HCl) or hydrogen bromide (HBr) within the combustion gases to render elemental mercury (Hg^0) to its soluble oxidised form (Hg^{2+}) such that it can be retained by wet-FGD scrubbers.

- **Sorbent-containing oxidants**
PAC-based sorbents as above which have been brominated or contain calcium bromide.

- **SCR oxidation**
This technology exploits the existing oxidant properties of selective catalytic reduction (SCR) systems installed primarily to control NO_x to co-oxidise Hg^0 to Hg^{2+} which is easier to retain in existing wet-FGD scrubbers.

- **Heavy metals-chelating agents**
Nitrogen or sulphur bidentate ligand-containing compounds delivered into the wet-FGD systems, which may be used in isolation or conjunction with any of the aforementioned techniques to capture Hg^{2+} and prevent Fe/Fe^{2+}-induced reduction re-emission of Hg^0.

There are pros and cons with all of these, and especially from the perspective of a cement manufacturer, primarily because many of these technologies were devised for the power industry.

Dry sorbent injection has been around for some years and the technology is now well understood. When using ACI, provided adequate plant construction and safeguards are in place to prevent 'pyrophoric incidents', PAC can be used for both elemental and oxidised mercury. The downside is that sorption is a reversible process and the PAC must be quickly removed from the system to prevent heat and other agents such as SO_3 displacing it. Once removed, the spent sorbent then becomes a hazardous waste which must be appropriately disposed of. In the case of a mercury compound sorbed onto highly-coloured carbon, with the possibility of desorbing volatile mercury should it interact with other groundwater metals, this will entail containment and burial in accordance with local regulations. Coal-fired power plants have landfill waste facilities where they dump their existing bottom ash and any unsalable flyash wastes. However, cement manufacturing facilities tend not to create such volumes of solid wastes and thus spent dry sorbent disposal may be an unwanted problem. In addition to solid waste handling issues, installation of a dry sorbent system will usually necessitate retrofitting of dry sorbent injection and an ESP or baghouse, with significant capital expenditure. Consequently, whilst dry sorbent technology works, it represents a high-cost solution.

Coal-fired power plants burn fuel to raise steam to drive turbines and for cooling. Their wet-FGD systems alone typically consume 3t water/MW/day, but their other water usage is several times that. Consequently they are strategically located close to abundant water supplies. In comparison, cement kilns, even those using wet-FGD systems, have historically not been major consumers of water and are less likely to have been sited close to abundant water sources or indeed have the same water treatment infrastructure as major power plants. It follows that from a cement manufacturer's perspective a mercury control system should preferably be dry and generate minimal solid residues with a low cost of disposal, or better still, generate residues that might be usable as product raw material.

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A critical difference between mercury emissions from coal-fired power plant and cement kilns is that power plants release their mercury steadily and broadly in line with their coal combustion. Kilns with in-line raw mills, however, route the kiln exhaust gases to the raw mill to dry the raw meal in order not to waste energy. When the raw mill is on, a large portion of the mercury exhausted from the kiln is fed back into the raw mill. The majority of mercury in particulate dust is recaptured at the raw mill, resulting in lower levels of mercury at the stack when the raw mill is on. When the raw mill is off, accumulated mercury is released and emitted as a short sharp release through the stack.[4,5] It follows that whilst mercury release from cement kilns to the environment is far less than the power sector, its releases are generally shorter in duration but higher in concentration. Therefore, any mercury emission abatement system for cement kilns may only need to function periodically but must be able to handle sharp spikes in release and be coordinated with the raw mill cycle.

Until recently there has been a growing trend in the coal-fired power sector to add calcium bromide into coal to create HBr in the combustion gas and thereby oxidise elemental mercury for retention of soluble mercury salts in the scrubber. Although this is a cheap method of preventing mercury going up the stack, it transfers soluble mercury pollution load to the plant waters. Moreover, HBr is corrosive to most metals, not just mercury, and significant in-situ corrosion has been observed at plant level. Lab studies have confirmed these observations with corrosion rates of approx 0.1mm in 180 days by 51ppmv HBr (a typical dose rate for a coal-fired plant) in lab exhaust gas at 300°F (149°C) for AISI 1008 cold-rolled steel.[6] The bromine corrosion scale has been found to be friable and non-protective. Also, at such doses of $CaBr_2$ on coal to achieve 50ppmv HBr, elemental bromine (Br_2) can co-occur in the flue gas.[7] Br_2 is a biocide, whose discharge to the environment is regulated, also transfers to plant water with the oxidised mercury, so both must be addressed with suitable water treatments.

There are a number of chelating agents on the market for removal of mercury from plant waters. Not all have been long-term tested for environmental stability and some based on carbon disulphide or carbon disulphide donors are restricted for use and/or sale by various state, national and supranational regulations.

The way power plants manage their wet FGD systems is of particular importance to cement manufacturers as they and wallboard makers are the principal buyers of gypsum byproduct from the power utility sector. Naturally, any process change delivering potential pollutants, their process residues, or spent sorbent into plant waters will impact the quality of byproduct gypsum and as a result, alter the product risk for the cement manufacturer. As such, whatever

Table 1: PRB bituminous blended coal-spiked combustion gas outlet total mercury vs CyCurex dosage

CyCurex	Test run (µg/Nm³)						
(gals/mscf)	27a	28a	28b	29a	29b	30a	30b
0.00	56.88	61.82	57.5	117.75	101.4	906.06	1005.7
0.52		19.17	22.5	48.29	44.3	678.95	
1.05	9.27	17.67		43.22		519.90	
1.57		15.38		34.72		363.50	
2.09	6.63						
2.62							
3.14	5.88						
9.66							91.7

Notes:
- *coal spiked at 1mg Hg/lb*
- *approximate residence time: 1-2s*

Table 2: PRB bituminous blended coal-spiked combustion gas – CyCurex process residue heavy metals analysis

Heavy metal	*Total metals (mg/kg)*	*Leachable metals by UK-NRA, TCLP eq procedure (mg/l)*	*TCLP limit 40CFR Part 261.24 (mg/l)*
Antimony	0.72	0.00055	1.0
Arsenic	4.2	0.00084	5.0
Cadmium	<0.20	<0.00020	1.0
Chromium	690	0.0017	5.0
Copper	47	0.020	na
Lead	5.0	0.0052	5.0
Mercury	67	0.0012	0.2
Nickel	350	0.26	10.0
Selenium	29	0.11	1.0
Zinc	25	<0.0060	700

Note: coal spiked at 1mg Hg/lb

treatment system is employed, it must not just remove mercury from exhaust gases but sequester that mercury, such that if transferred to byproduct gypsum dihydrate it remains both stable to leaching and importantly to the onward high temperature processing of gypsum by wallboard and Portland cement manufacturers.

Technology overview

Cylenchar Ltd's CyCurex® is a generic reagent system for the remediation of toxic heavy metals-contaminated materials. The risks of harm from toxic heavy metals wastes are dramatically increased if they are in soluble or latently-soluble forms. CyCurex treatment converts soluble metal compounds into stabilised metal sulphides. The sulphide ores of heavy metals are stable and amongst the most insoluble of heavy metal compounds. Therefore, they are of dramatically lower toxicity and greater stability than their other adducts. This stability is why sulphide metal ores are so abundant in nature. As so many heavy metals are derived from their sulphide ores, it is reasoned that Cylenchar technology acts to revert these materials back to the form in which nature intended them.

CyCurex can bind and stabilise a broad spectrum of heavy metals in a wide variety of substrates and eliminate or reduce metals leaching to within internationally accepted regulatory limits, thereby preventing contamination of soil and/or groundwater. Treated soils can be rendered compliant with US-EPA-Universal Treatment Standard (UTS) Limits and EU Waste Acceptance Criteria (WAC) limits set out in WAC Directive 2003/33/EC and derived from Directive EU 1999/31/EU. Treated materials will pass testing by US-Toxic Characteristic Leaching Procedure (TCLP), DIN38,414S(4), UK-NRA, UNI 10802.A.2 and EN12457 methodologies.

Cylenchar has developed its CyCurex technology to address heavy metals sequestration of combustion gases from coal-fired power plants, cement kilns and waste incinerators, chemical waste combustion, exhaust gases from metals processing and oil field off-gases. It can be deployed as an induct spray, dry scrubbing agent or simply piggy-backed into an existing wet-FGD system as a low level additive.

Dry scrubber testing

Process trials of CyCurex were conducted at 1MW level in dry scrubber application with mercury-spiked coal combustions gases modelling cement kiln discharges, at the Southern Research Institute (SRI) Combustion Research Centre at Birmingham, Alabama, USA. Results showed that the technology can rapidly and directly remediate moderate and high concentrations of both oxidised and elemental mercury in exposure times as low as 1-2s at dose levels making it highly cost competitive vs PAC (see Table 1).

In a coal combustion gas stream carrying a concentration of 1000µg/Nm³ total mercury and at least 34µg/Nm³ of elemental mercury, CyCurex was easily able to reduce the total mercury concentration by over 90 per cent and deal with over 75 per cent of the elemental mercury, demonstrating that the technology can cope with high level spikes in emission.

Moreover, leaching studies on process residues, which are largely gypsum with trace coal ash residues, showed that mercury and a broad spectrum of other heavy metals had been sequestered to within internationally-accepted leaching norms (see Table 2).

Additionally, heat testing to >380˚C has shown no release of mercury, thereby illustrating stability of the sequestered metals compounds and non-detrimental effect on potential byproduct gypsum.

SRI Process residues are primarily calcium sulphite-sulphate adducts and calcium thiosulphate, plus traces of calcium phosphates.

Additionally they contain fly-ash components, potassium and calcium iron (Fe^{2+}/Fe^{3+}) alumino silicates, plus low-level traces of particulate carbon.

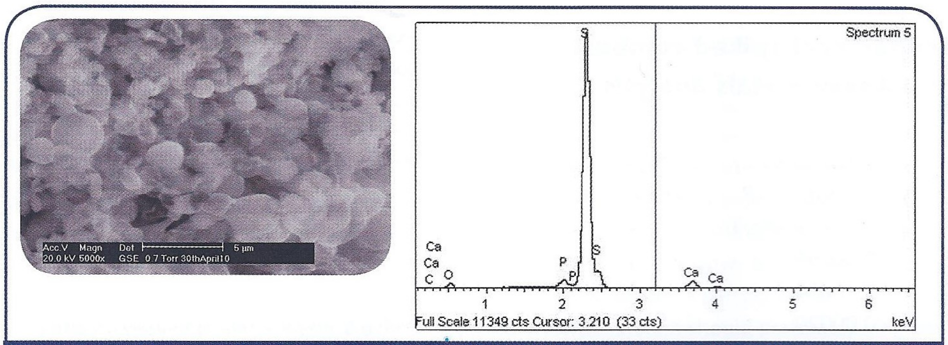
Wet scrubber testing and application

Cylenchar's technology has been licensed in North America and has been undergoing pilot trials and in-situ testing in wet FGD systems in several US coal-fired power plants in the 400-660MW range. Results of recent testing at Owensboro Municipal Utilities (OMU), Elmer Smith Power Station, located in Owensboro, Kentucky, were reported at the Power Plant Pollutant Control "MEGA" Symposium, Baltimore, Maryland, on 19 August 2014.[8]

OMU has a combined total power output of 433MW:

- Unit 1 is a 151MW B&W Cyclone Unit built in 1964. This unit has over-fire air (OFA) and an SCR for NO_x control. The SCR is a 2+1+1 Layer design with a designed NO_x removal of 90 per cent from 0.7lb/mBtu inlet. Flue gas flows through a regenerative air heater and into an ESP.
- Unit 2 is a 282MW CE tangentially-fired unit built in 1974. This unit has low-NO_x burners (LNB) with separated over-fire air (SOFA) and a Hamon selective non-catalytic reduction (SNCR) system for NO_x control. Flue gas flows through a regenerative air heater and into an ESP.

The plant has a combined Wheelabrator Wet-FGD for units 1 and 2. The W-FGD is



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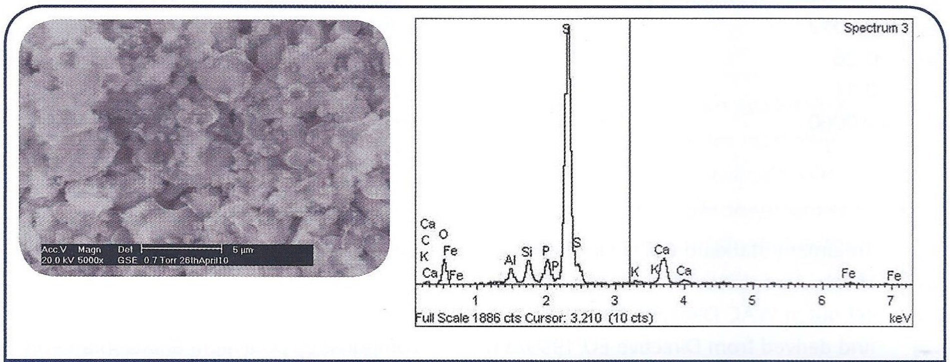

SRI process residues also contain fly ash components, potassium and calcium iron alumino silicates, plus low level trace of particulate carbon

a limestone scrubber with forced oxidation and is designed for 97 per cent reduction of inlet SO_2 levels. The plant burns a Southern Illinois Basin Coal mined locally with a 2-4 per cent sulphur content.

Under normal operating conditions, the elemental mercury (Hg^0) at the Scrubber Inlet over the three-day baseline period was between 5-10µg/Nm^3. The scrubber inlet Hg tends to be one half to two-thirds Hg^0 during the day and then during the night this ratio flips and it is as much as two-thirds oxidised mercury (Hg^X).

The stack total mercury is mostly all elemental and runs between 4-12µg/Nm^3 with occasional numbers above 12µg/Nm^3. The average scrubber capture rate for mercury over a daily cycle is around 29 per cent.

On commencement of reagent dosing, even at the lowest injection rates of 48gal/h, the reagent retained better than 98 per cent of the oxidised Hg^X and captured as much as 55 per cent of the elemental Hg^0. At the highest injection rate of 240gal/h, the capture rate of Hg^0 exceeded 75 per cent with continued retention of Hg^X at 98 per cent or more.

The reagent had no negative impact on the scrubber solids or sulphite levels. OMU sells its gypsum for wallboard and the reagent will have no adverse impact on the quality and saleability of the gypsum.

From an operational perspective, OMU runs its scrubber with chloride levels between 500-1500ppm and its blow-down is typically 50 per cent open. Sulphite levels are monitored both in the absorbers and the gypsum. During the entire test period, no changes were observed in any of the key operational parameters.

Subsequent trials at OMU have shown that the reagent can be used in tandem with calcium bromide as well as existing SCR/SNCR and oxidation systems.

Water and solids samples analysis – other heavy metals

OMU discharges its scrubber slurry into two Dorr-Oliver 60' D type thickeners. The overflow liquors are continually recycled back into the scrubber either as make-up water or to feed the scrubbers limestone slurry mills. Gypsum slurry concentrate from the thickeners is pumped to two Komline-Sanderson KS-ADPEC 2.5ft x 21ft Vacuum Belt Filters. Isolated gypsum solids are given a cursory on-belt wash with clean water, then conveyed as damp solid to storage.

Samples of thickener gypsum slurry and isolated gypsum have been assessed for heavy metals content and leaching across a broad spectrum of metals of concern (see Table 3). The analyses for the Baseline reflects the internal scrubber baseline conditions of 6 June and the Run period of 11 June. Weighting the reagent run data against baseline total metals loading, indicates that the content of all soluble heavy metals of concern in the gypsum mother liquors from the gypsum slurry thickener had been reduced by an overall average of 40 per cent. Residual soluble metals in the isolated gypsum had been reduced by more than 40 per cent, relative to total metals content. These reductions in soluble metals

Mercury control through scrubbers

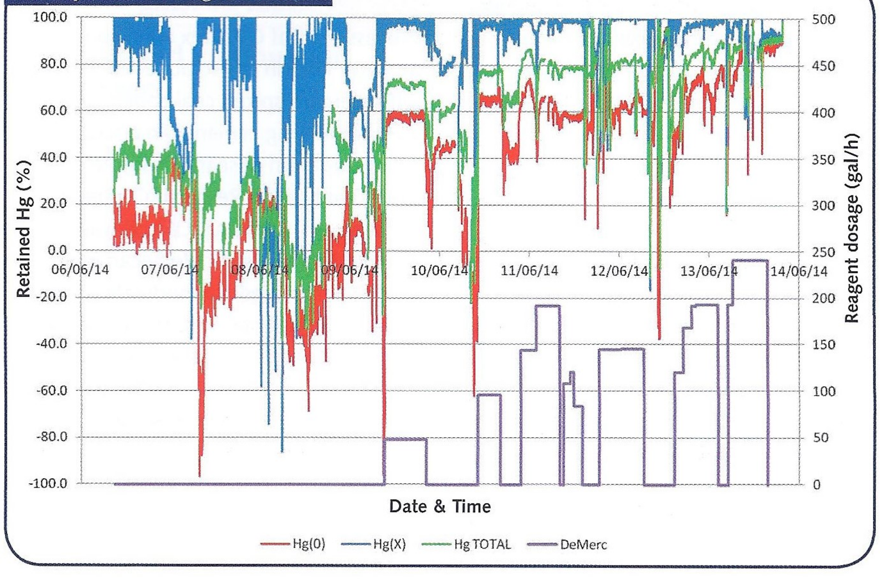

Table 3: OMU gypsum metals analysis

Heavy metal	Gypsum thickener slurry Total metals (mg/kg DW)		Soluble metals (mg/l)		Gypsum solid Total metals (mg/kg DW)		Leachable metals (mg/l)		TCLP limit 40CFR Part 261.24
	Baseline	Run	Baseline	Run	Baseline	Run	Baseline	Run	
Antimony	ND	ND	ND	ND	0.083	0.0465	ND	ND	1.0
Arsenic	15.10	11.30	4.84	2.50	5.37	3.39	0.0161	0.0101	5.0
Beryllium	ND	ND	ND	ND	0.0415	0.0295	ND	ND	
Cadmium	0.99	1.90	0.32	0.34	0.161	0.2345	0.0076	0.0048	1.0
Chromium	43.70	32.70	13.95	7.17	26.85	22.7	0.0165	0.0079	5.0
Cobalt	ND	ND	ND	ND	0.1825	0.0925	ND	ND	
Copper	2.78	2.81	0.90	0.59	0.989	0.824	0.2220	0.1655	N/A
Lead	2.25	1.61	0.72	0.36	0.7665	0.662	ND	ND	5.0
Manganese	70.30	85.85	22.45	15.55	16.05	5.085	0.2810	0.0660	
Mercury	0.56	1.15	0.18	0.26	0.0798	0.389	ND	ND	0.2
Nickel	5.33	8.26	1.71	1.54	1.4	1.185	0.0290	0.046	10.0
Selenium	17.70	34.75	5.69	6.20	4.15	4.185	0.0337	0.0187	1.0
Zinc	47.25	69.15	15.10	12.95	11.95	11.085	0.3920	0.1045	700
Total	**205.96**	**249.47**	**65.84**	**47.45**	**68.07**	**49.91**	**0.9978**	**0.4281**	

loading are significant especially given the comparatively short duration of the reagent dosing run, the variable delivery of heavy metals into the system and historical build-up of soluble metals in the scrubber waters prior to the start of the trial.

System economics

OMU was planning to install an Hg oxidation system that would apply a chemical on the coal belt, a dry sorbent injection (DSI) system for lowering the SO_3 content going into the ACI system, an ACI system and a Hg re-emission suppression reagent system at the scrubber. Using Cylenchar technology in conjunction with a Hg oxidation additive on the coal belt, OMU has the possibility to meet US Mercury and Air Toxics Standards (MATS) without a DSI and ACI system. This offers the opportunity to create considerable cost savings in terms of both capital and operating expenses. OMU's capital cost savings from not installing a DSI and ACI system could be in the range of US$2-4m and reduce total annual operating costs to roughly 40-50 per cent of its original MATS compliance cost estimates, thereby providing a potential annual cost savings of between US$3-3.5m.

Summary

Cylenchar's CyCurex system is an inorganic sulphide-based metals capture and sequestration technology with the following key features:

- inorganic reagent, comparatively safe and non-toxic to handle, with no toxic degradation products
- suppresses mercury re-emission from wet-FGD systems
- retains over 98 per cent of oxidised mercury
- can capture between 50-75 per cent of elemental mercury at the same time
- can capture 50 per cent of the elemental Hg with extremely low injection rates
- will work in tandem with mercury oxidant systems
- can capture and sequester a broad spectrum of heavy metals simultaneously
- has no major water demands and creates little solid waste, if any
- residues meets all TCLP standards
- does not impair byproduct gypsum quality
- reduces the metals leaching from gypsum, thereby improving product quality and de-risking byproduct gypsum sold into wallboard and cement manufacture
- offers tremendous capital and operating cost savings over existing technologies.

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