Worldwide Pollution Control Association

WPCA-Duke Energy FGD Wastewater Treatment Seminar

March 7, 2013

WPCA

Visit our website at www.wpca.info

Options for Managing Dissolved Solids from FGD Wastewater

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7 March 2013

Agenda

- Background and context
- FGD wastewater processes
- Promising options
- Leachability methods for vetting options

Context

1982

Steam Electric Power Generating Effluent Guidelines last revised

2005

Annual review spotlights industry, recommends further study

2009

Effluent Point Source Category: Final Detailed Study Report

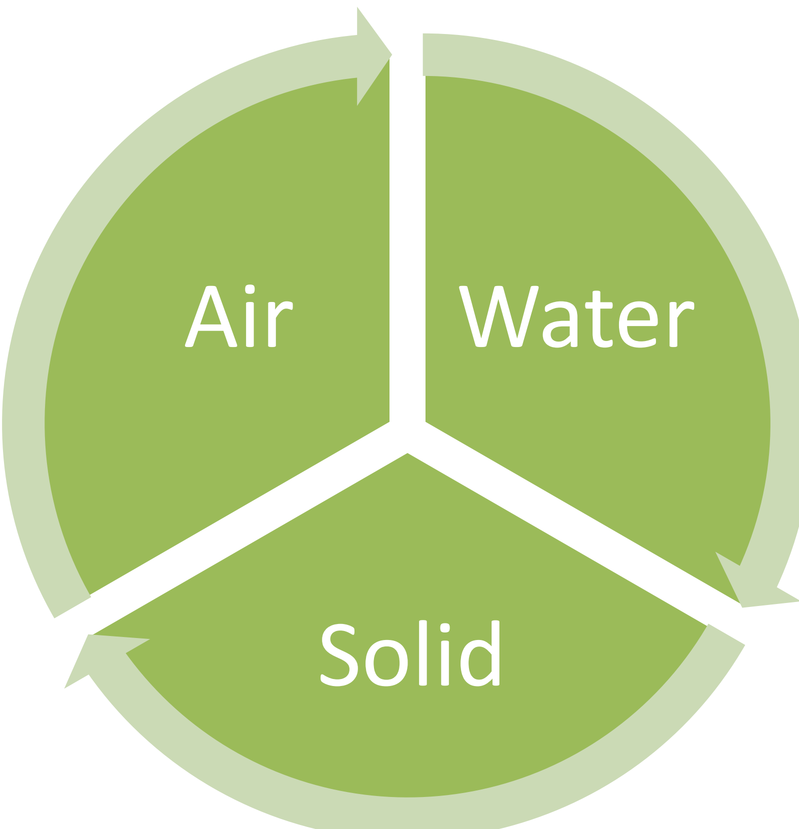
2012

EPA agrees to sign a decision taking action by May 22, 2014

February 8, 2013

EPA provides status report – interagency review ongoing

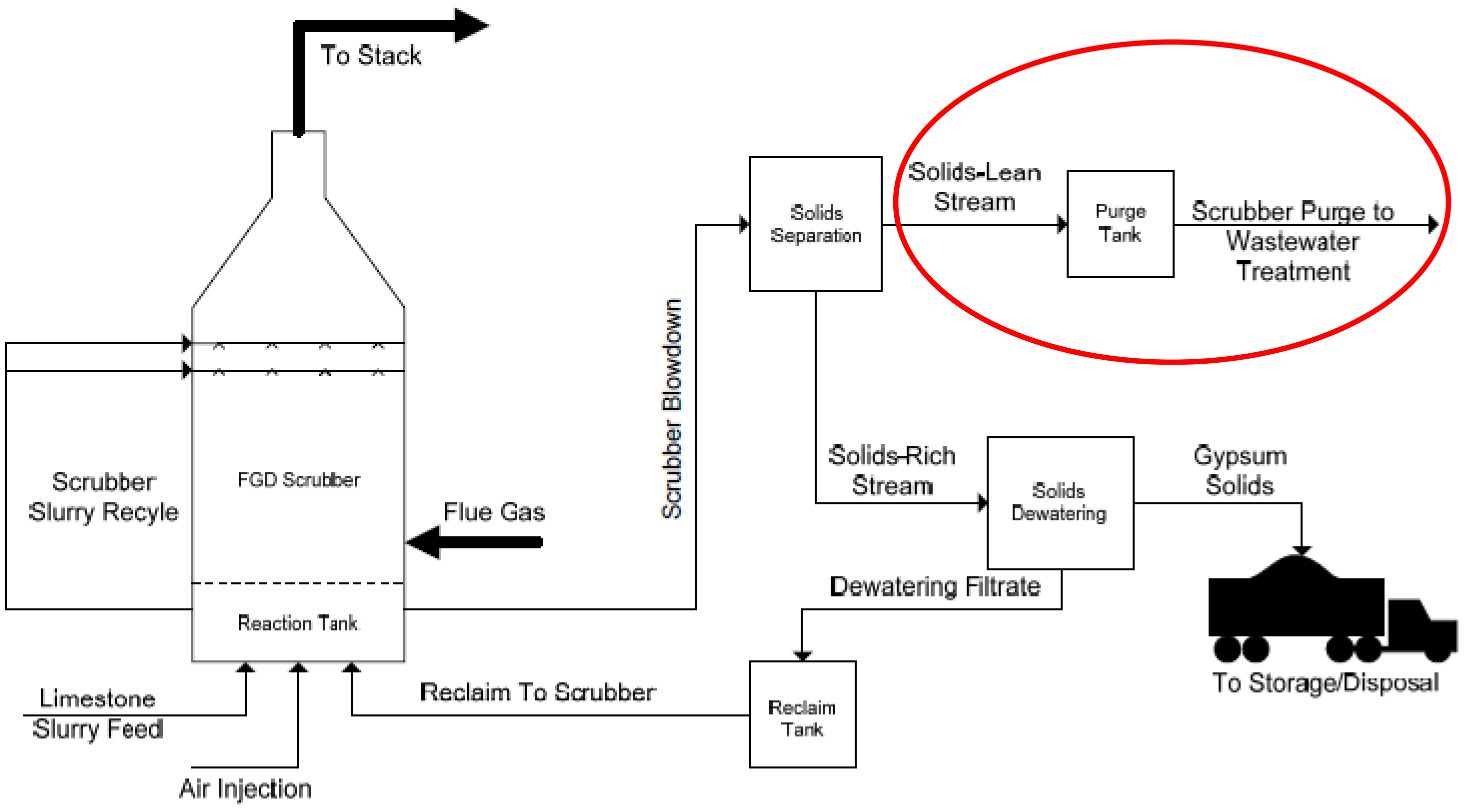
Trend: Contaminant Sequestration into Solid Phase



Steam Electric Power Generating Point Source Category: Final Detailed Study Report

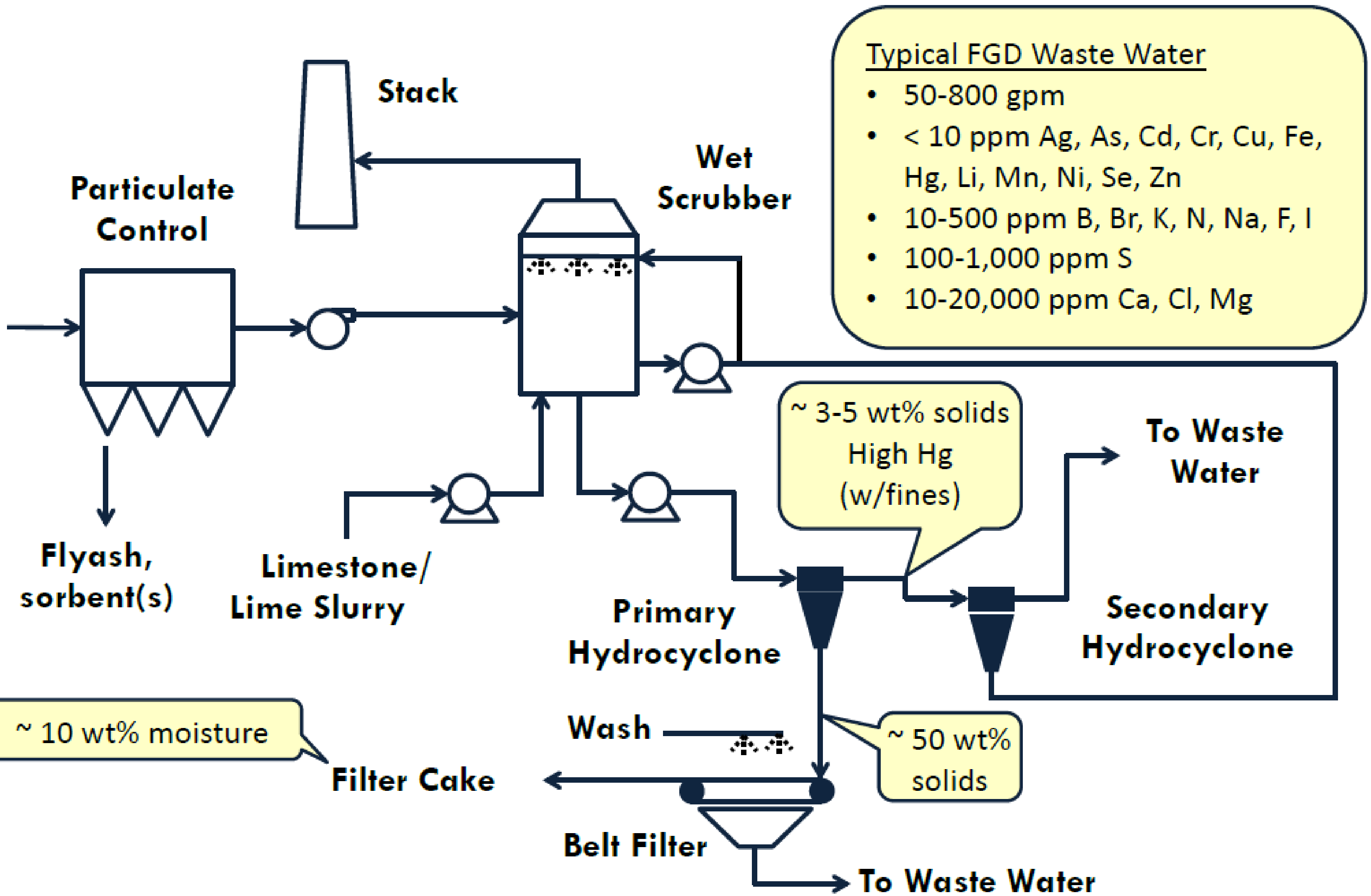
October 2009

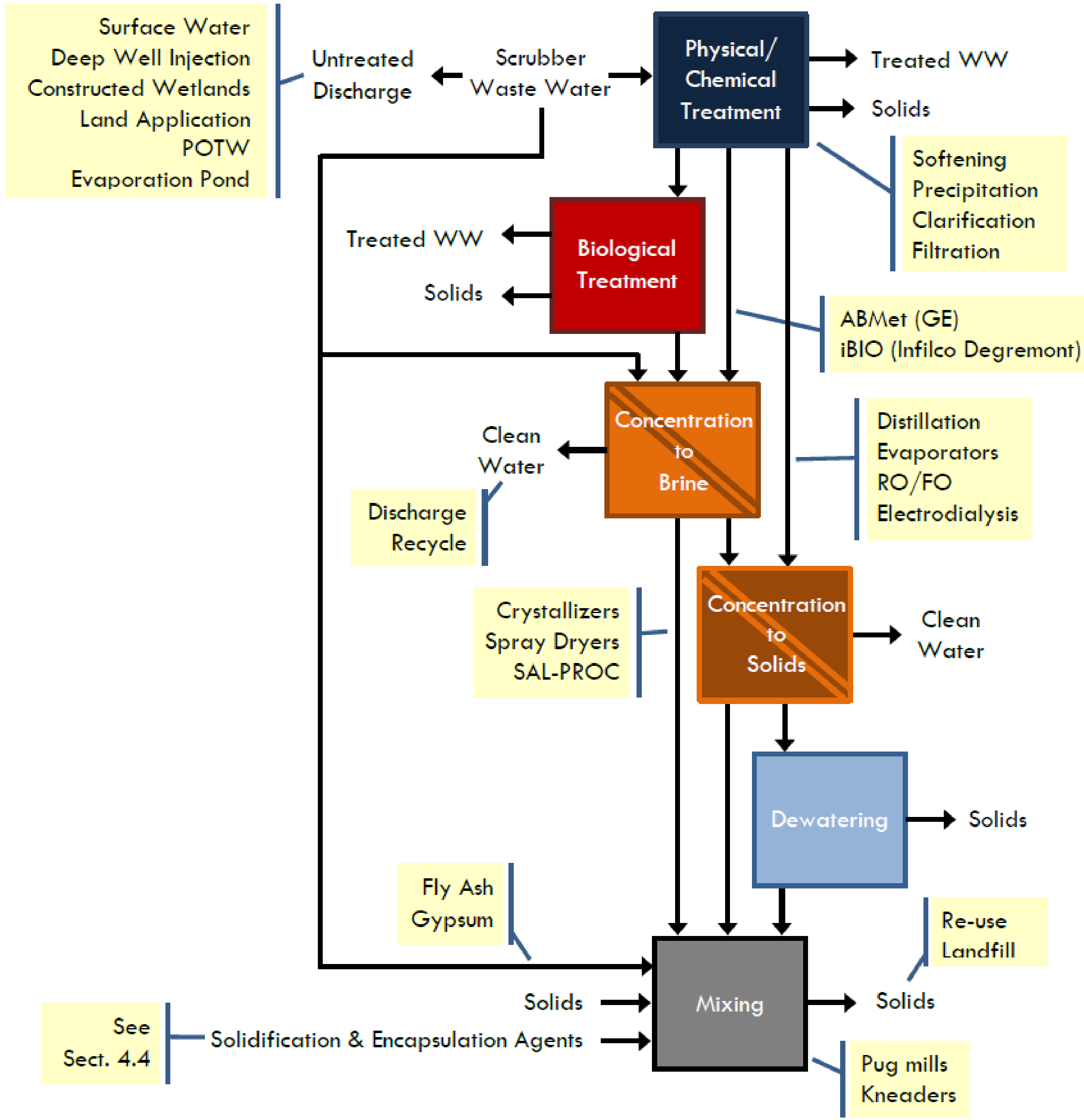
General Process Flow



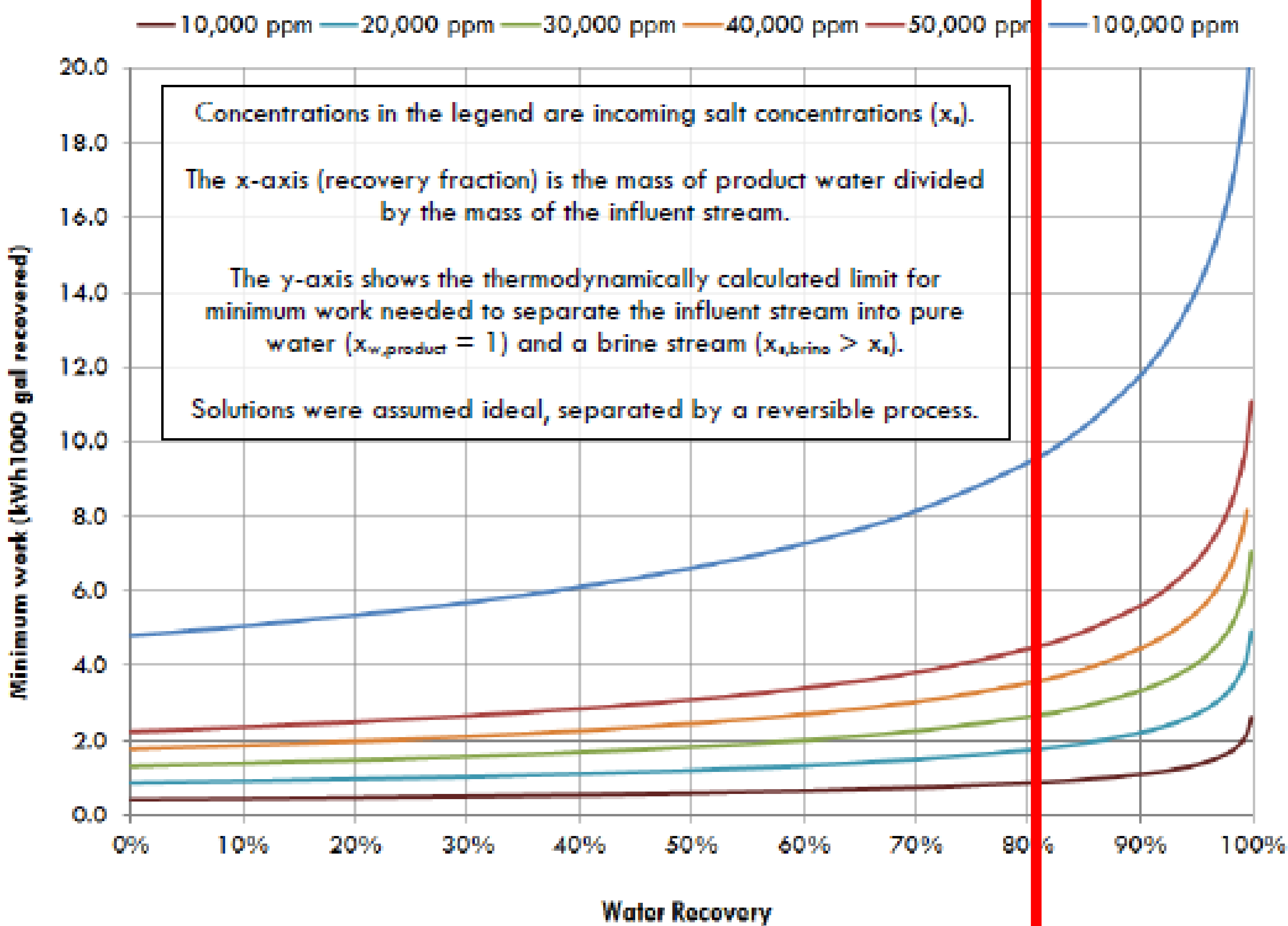
Source: SEPG Point Source Category: Final Detailed Study Report

Scrubber Blowdown vs. Wastewater



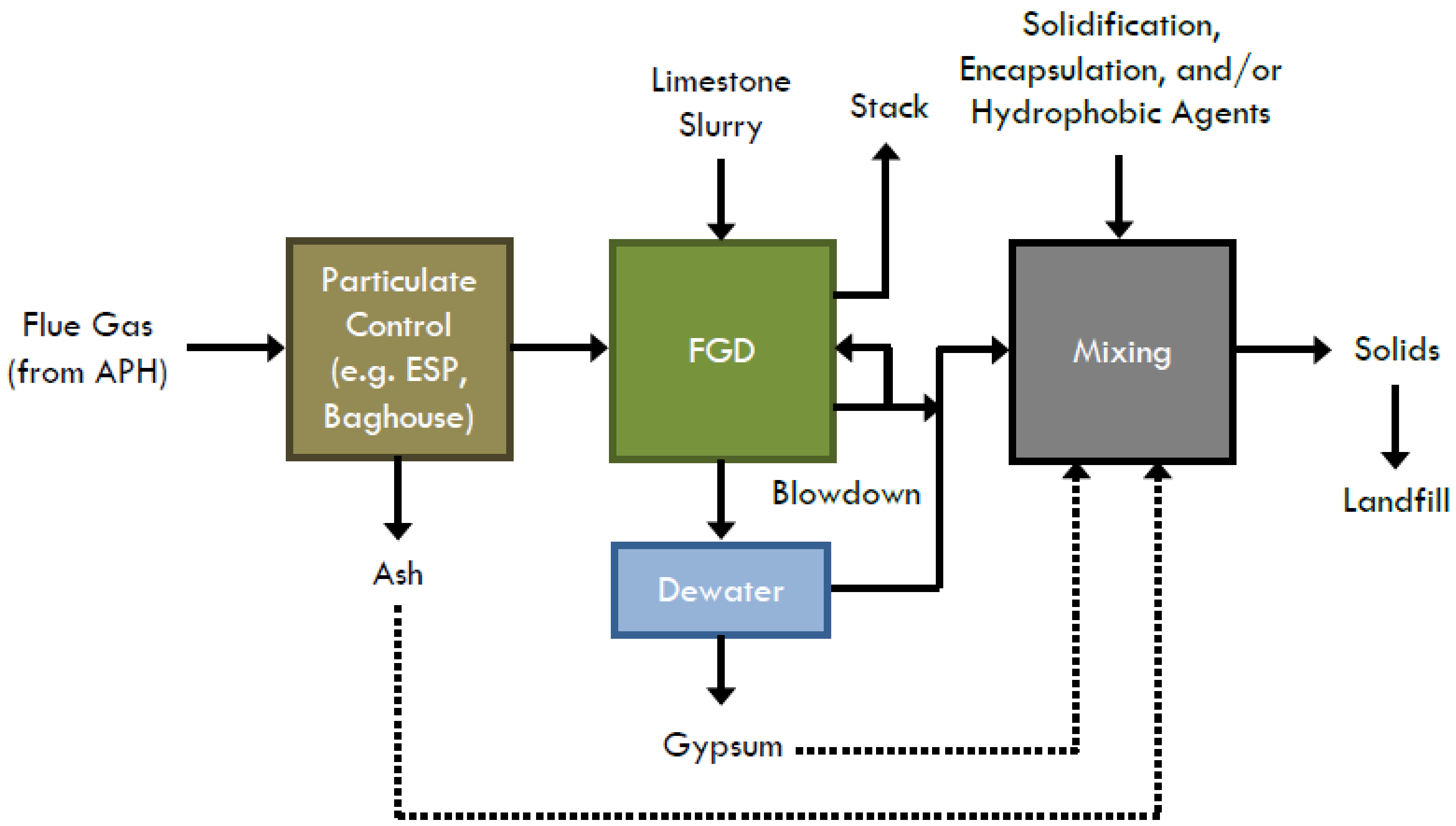

Surface Water
Deep Well Injection
Constructed Wetlands
Land Application
POTW
Evaporation Pond
Untreated Discharge
Scrubber Waste Water
Physical/ Chemical Treatment
Treated WW
Solids
Softening
Precipitation
Clarification
Filtration
Treated WW
Solids
Biological Treatment
ABMet (GE)
iBIO (Infilco Degremont)
Clean Water
Concentration to Brine
Distillation
Evaporators
RO/FO
Electrodialysis
Discharge
Recycle
Crystallizers
Spray Dryers
SAL-PROC
Concentration to Solids
Clean Water
Dewatering
Solids
Fly Ash
Gypsum
Re-use
Landfill
Solids
Mixing
Solids
See Sect. 4.4
Solidification & Encapsulation Agents
Pug mills
Kneaders

	Assumptions	Calculations
Scrubber WW Production	• 600 gpm (avg) *(estimate supplied by Duke)* • 8.34 lb/gal *(assumes much of the TDS and TSS removed in waste water and underestimates density to be conservative)*	600 gpm x 8.3 lb/gal x 60 min/h x 24 h/day = 7.21M lb/day *as scrubber waste water*
Concentrated Scrubber WW Production	• 85% water recovery *(e.g. from reverse osmosis)*	7.21M lb/day x 15% = 1.08M lb/day *as conc. scrubber waste water*
Estimated Plant btu Consumption	• 2,240 MW @ 37.8% heat rate *(from Duke external publications)*	2,240 MW x 24 h/day x 3.412×10^6 btu/MWh x (1/0.378) = 4.85×10^{11} btu/day *consumed from coal*
Estimated Fly Ash Production	• 11,500 btu/lb • 10% ash *(assume a relatively low btu bituminous coal with relatively high ash to be conservative – i.e. assume a lot of ash is available as fly ash)*	4.85×10^{11} btu/day x (1/11,500 btu/lb) x 10% ash = 4.22M lb/day *as fly ash*
Moisture wt% (WW + fly ash mix)	[wt waste water]/ [wt waste water + wt fly ash]	[7.21M lb/day]/ [7.21M lb/day + 4.22 M lb/day] = 63 wt% moisture *for WW+ash mix*
Moisture wt% (concentrated WW + fly ash mix)	[wt conc. waste water]/ [wt conc. waste water + wt fly ash]	[1.08M lb/day]/ [1.08M lb/day + 4.22 M lb/day] = 20 wt% moisture *for conc. WW+ash mix*

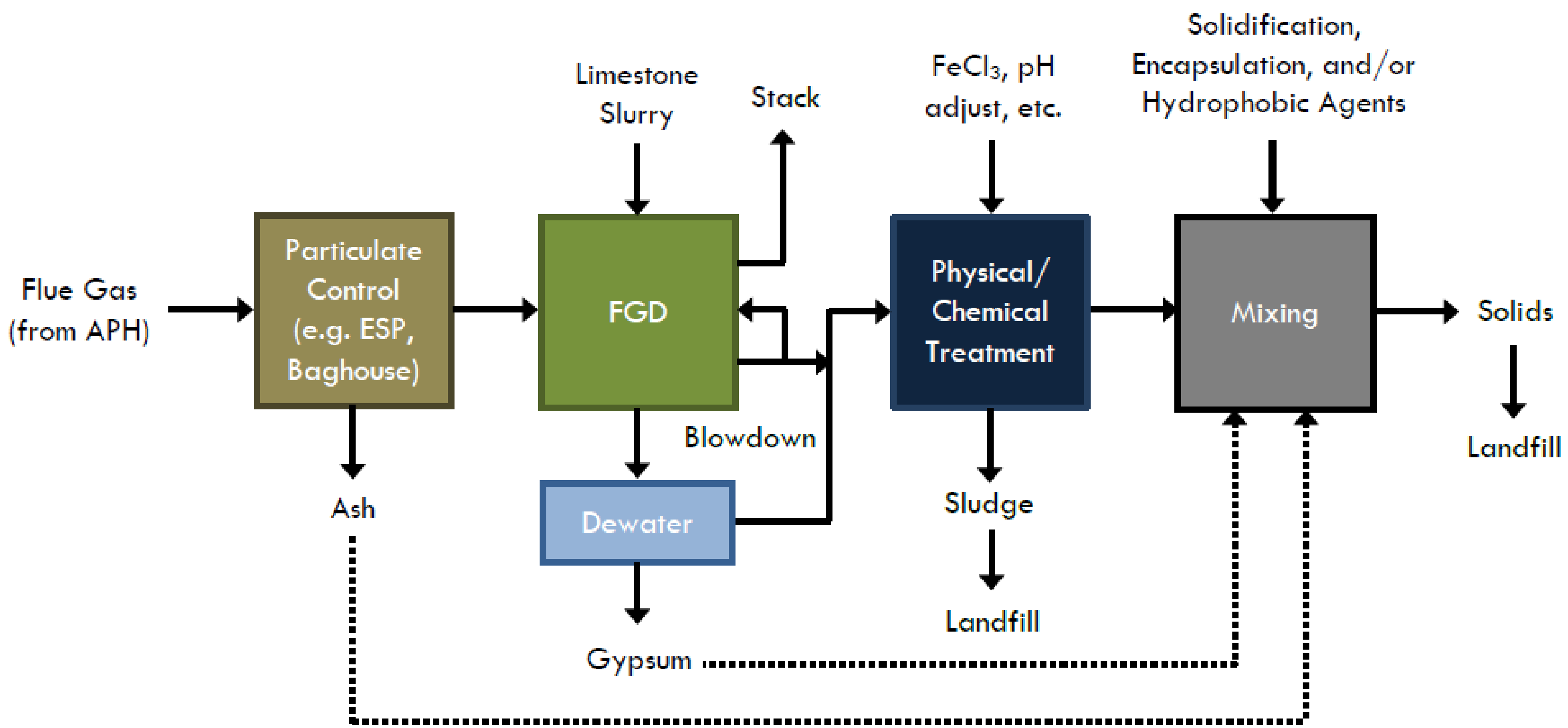


10,000 ppm
20,000 ppm
30,000 ppm
40,000 ppm
50,000 ppm
100,000 ppm
Concentrations in the legend are incoming salt concentrations (x_s).
The x-axis (recovery fraction) is the mass of product water divided by the mass of the influent stream.
The y-axis shows the thermodynamically calculated limit for minimum work needed to separate the influent stream into pure water ($x_{w,product} = 1$) and a brine stream ($x_{s,brine} > x_s$).
Solutions were assumed ideal, separated by a reversible process.
Minimum work (kWh1000 gal recovered)
Water Recovery
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
18.0
20.0
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%

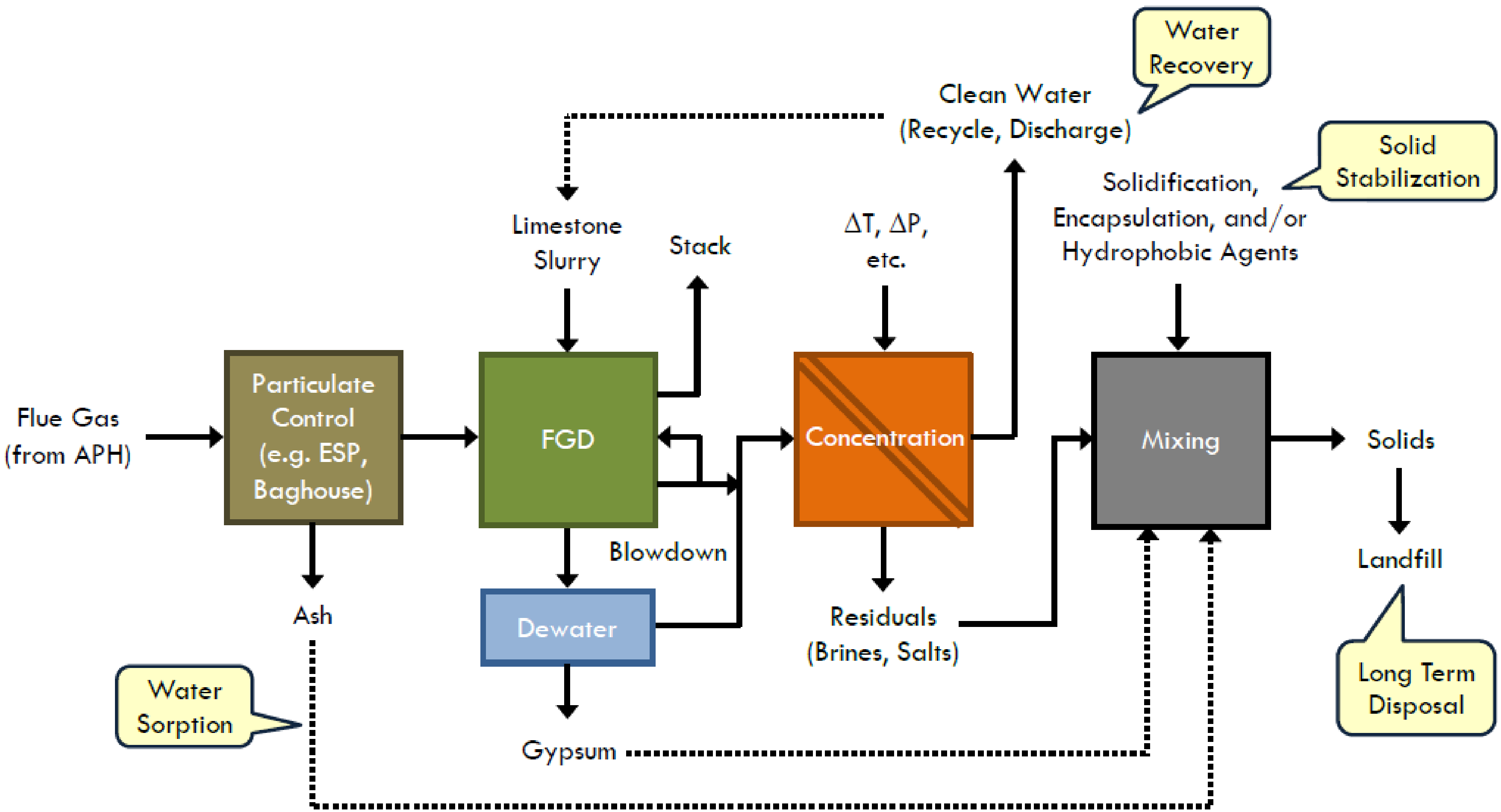
Solidification of Untreated WW



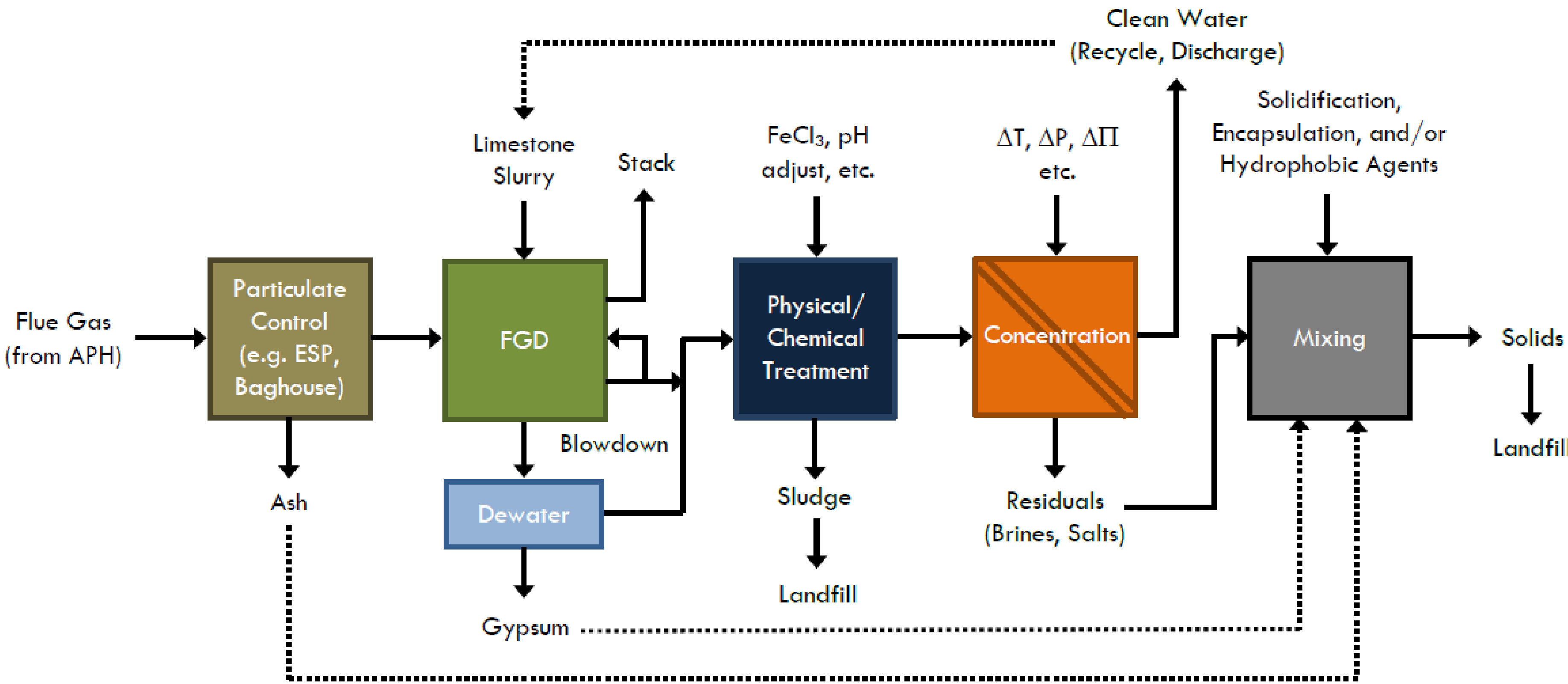
Solidification of Treated WW



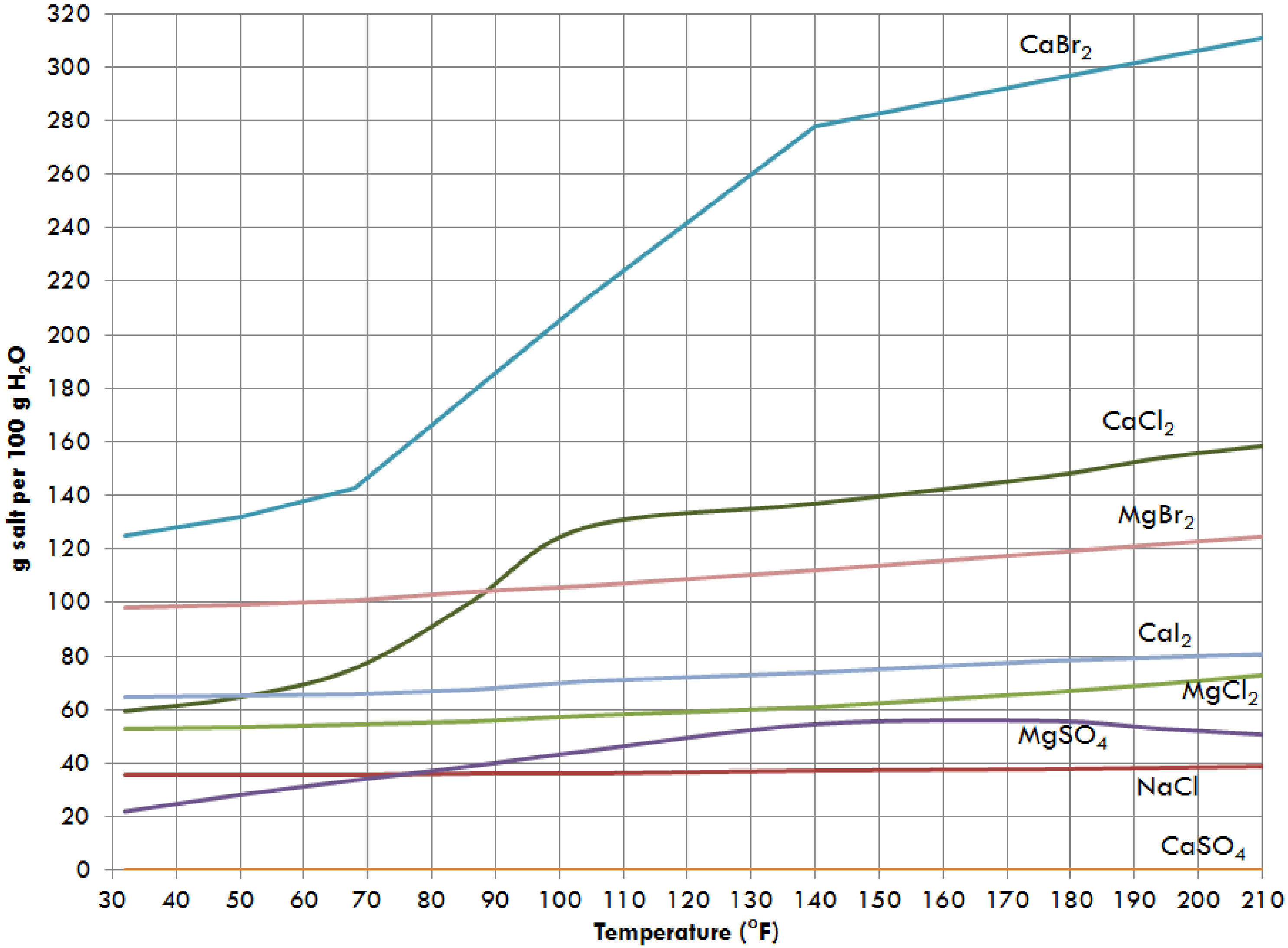
Concentrated, Untreated WW



Concentrated, Treated



Many constituents are quite soluble



Promising Options

- Poz-o-tec
- Geopolymer
- Organo-silanes
- Tegra-tuff
- Dolocrete

Poz-o-tec

- The mix proportion for Poz-o-Tec stabilization typically ranges from about 0.6 to 1 part fly ash to 1 part FGD material with up to 4% of dry weight lime added to the mixture.

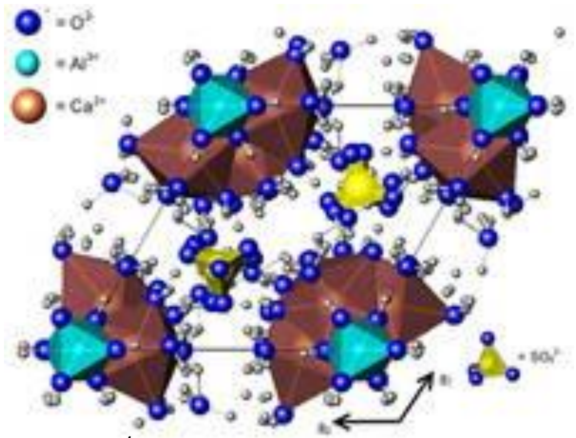
$SiO_2 + Ca(OH)_2 + H_2O \rightarrow CaO{\cdot}SiO_2{\cdot}2H_2O$

$Al_2O_3 + 4Ca(OH)_2 + 9H_2O \rightarrow 3CaO{\cdot} Al_2O_3{\cdot} Ca(OH)_2{\cdot}12H_2O$

$Fe_2O_3 + Al_2O_3 + 6Ca(OH)_2 + 6H_2O \rightarrow 6CaO{\cdot} Al_2O_3{\cdot} Fe_2O_3{\cdot}12H_2O$

Ettringite:

$2Ca(OH)_2 + 3CaSO_4{\cdot}2H_2O + CaO{\cdot}Al_2O_3 + 24H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O$

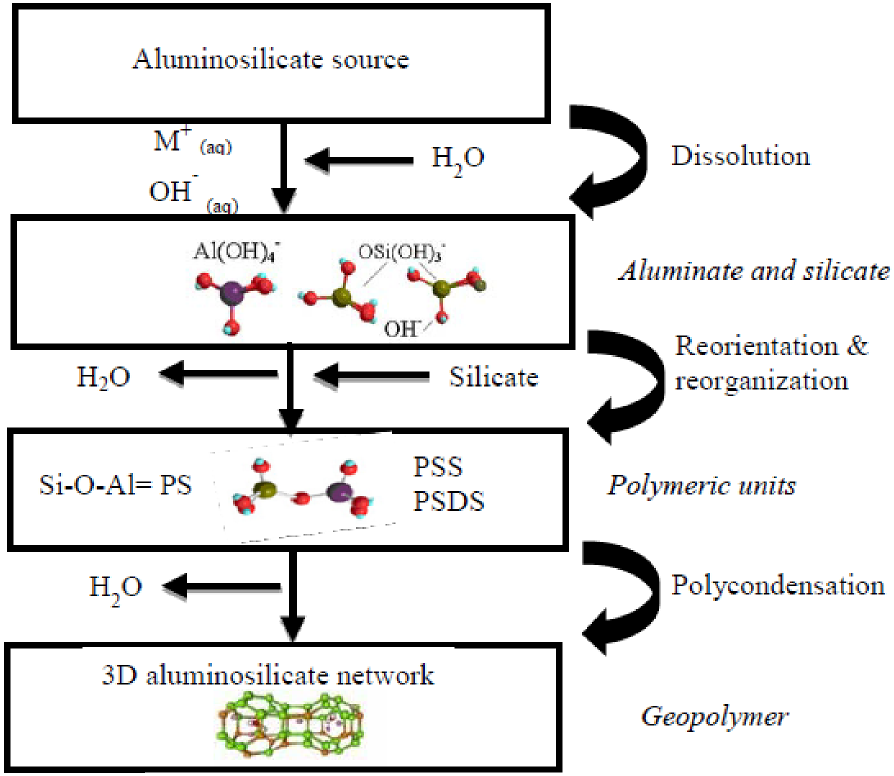


Source: http://www.gzn.uni-erlangen.de/en/applied-geosciences/applied-mineralogy/cement-mineralogy/pvaopc-interaction/

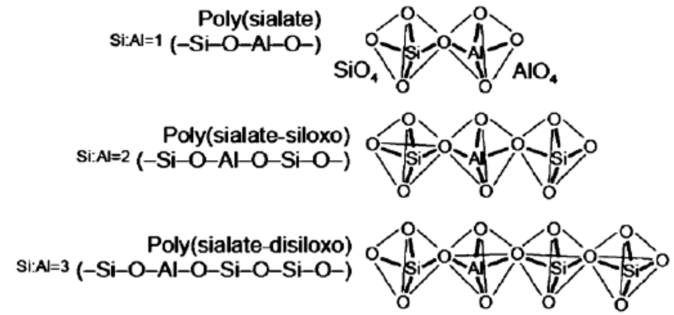
Use concentrated wastewater as molding moisture content

Mix and compact

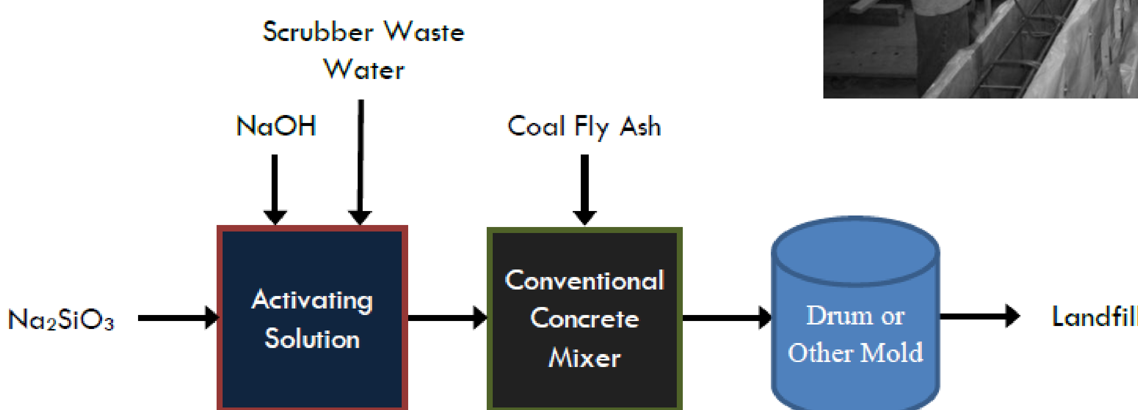
Geopolymer



Aluminosilicate source
M+ (aq)
OH- (aq)
H2O
Dissolution
Al(OH)4-
OSi(OH)3-
OH-
Aluminate and silicate
H2O
Silicate
Reorientation & reorganization
Si-O-Al= PS
PSS
PSDS
Polymeric units
H2O
Polycondensation
3D aluminosilicate network
Geopolymer

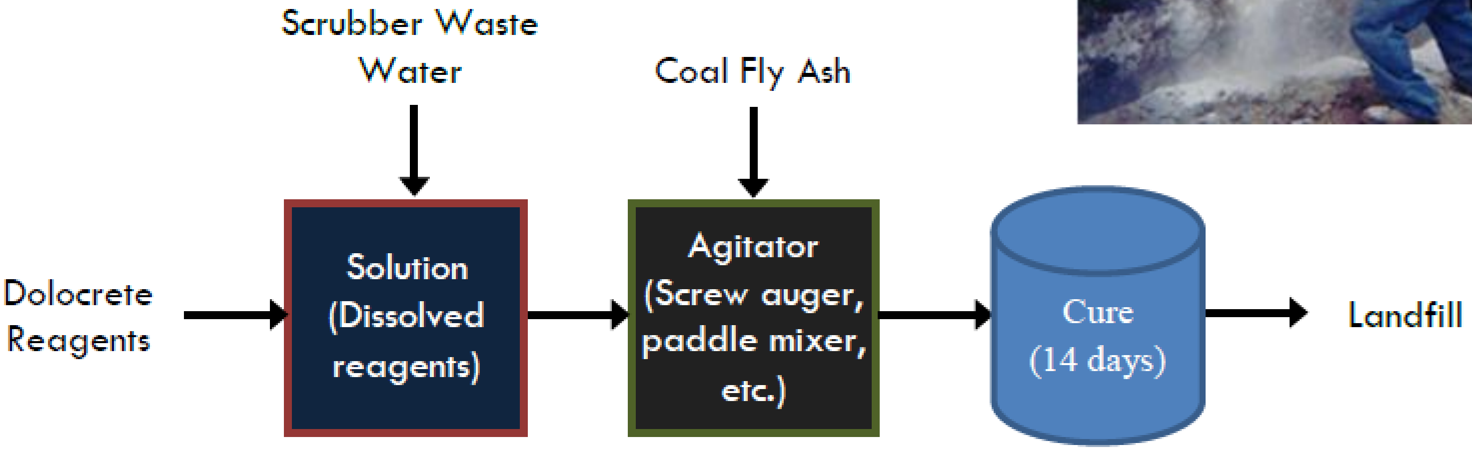


Poly(sialate)
Si:Al=1 (-Si-O-Al-O-)
SiO4
AlO4
Poly(sialate-siloxo)
Si:Al=2 (-Si-O-Al-O-Si-O-)
Poly(sialate-disiloxo)
Si:Al=3 (-Si-O-Al-O-Si-O-Si-O-)



Scrubber Waste Water
NaOH
Coal Fly Ash
Na2SiO3
Activating Solution
Conventional Concrete Mixer
Drum or Other Mold
Landfill

Dolocrete

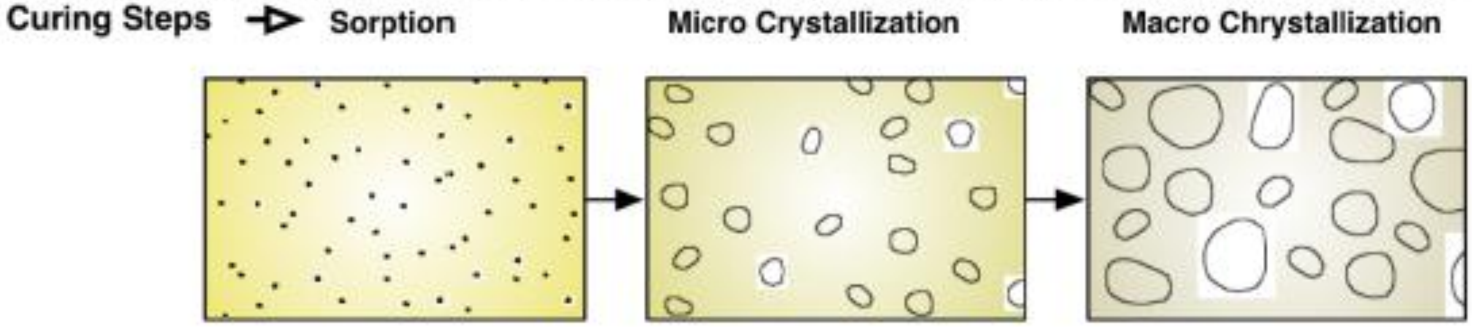


Magnesium oxide based binder, varies from 2:1 to 6:1, solid matrix to binder

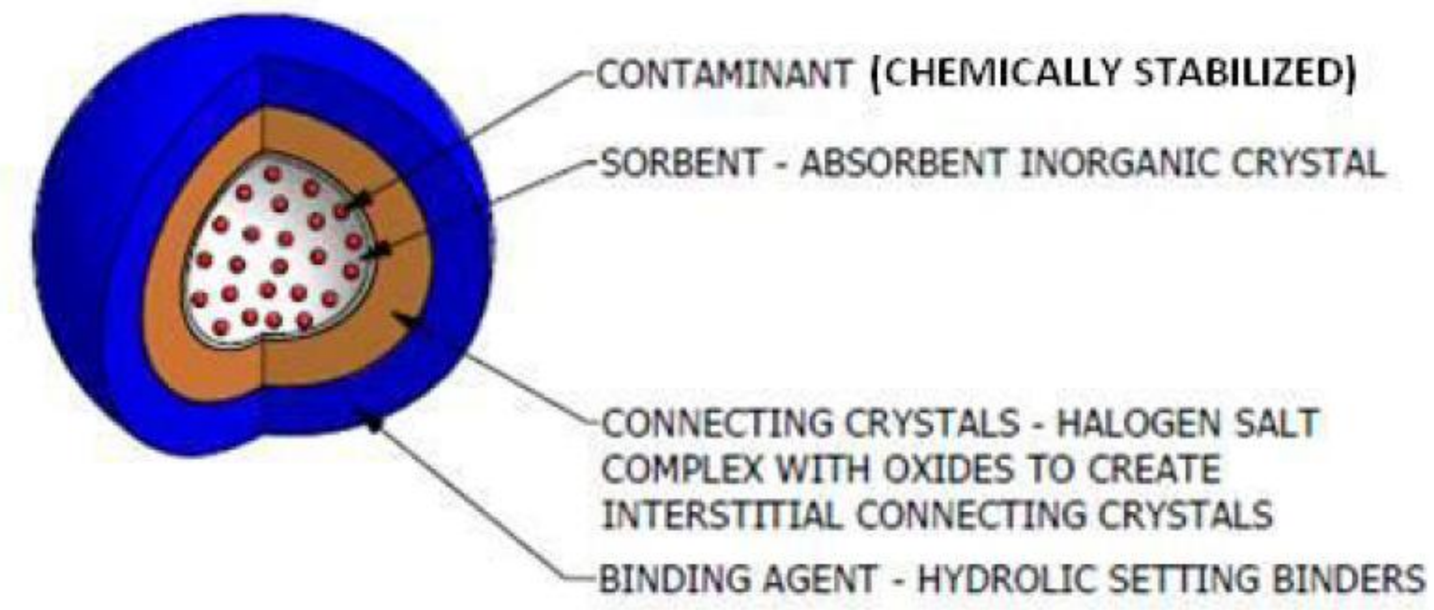
Tegratuff

TEGRATUFF™

A Low-Temperature Ceramic Process for Sorption, Immobilization and Binding of Leachable Wastes



Tegratuff


CONTAMINANT (CHEMICALLY STABILIZED)
SORBENT - ABSORBENT INORGANIC CRYSTAL
CONNECTING CRYSTALS - HALOGEN SALT COMPLEX WITH OXIDES TO CREATE INTERSTITIAL CONNECTING CRYSTALS
BINDING AGENT - HYDROLIC SETTING BINDERS

Tegratuff

- Mix ingredients to form solid or semi-solid
- Adjustable strength and permeability
- Ingredients are proprietary, mix design is modeled ahead of time

Tegratuff


Mixing Process
Treated “green” ash blocks
Use at other
Duke Plants
Off site non haz disposal
Treated Bulk non haz
On-site non haz disposal
FreeFoto.com

Organo-silanes

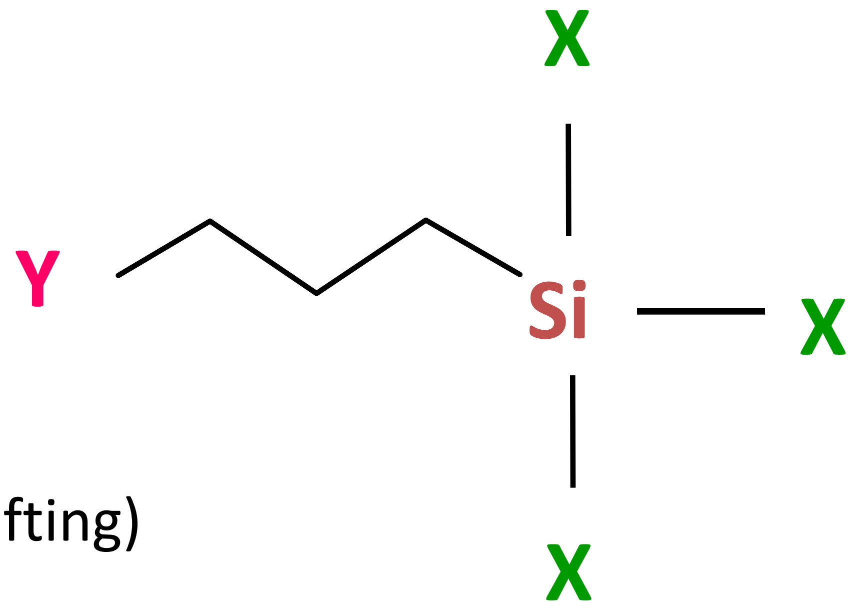
Clear and initially water soluble

Doesn't form a film

Doesn't bind particles together

Covalent bonding mechanism (grafting)

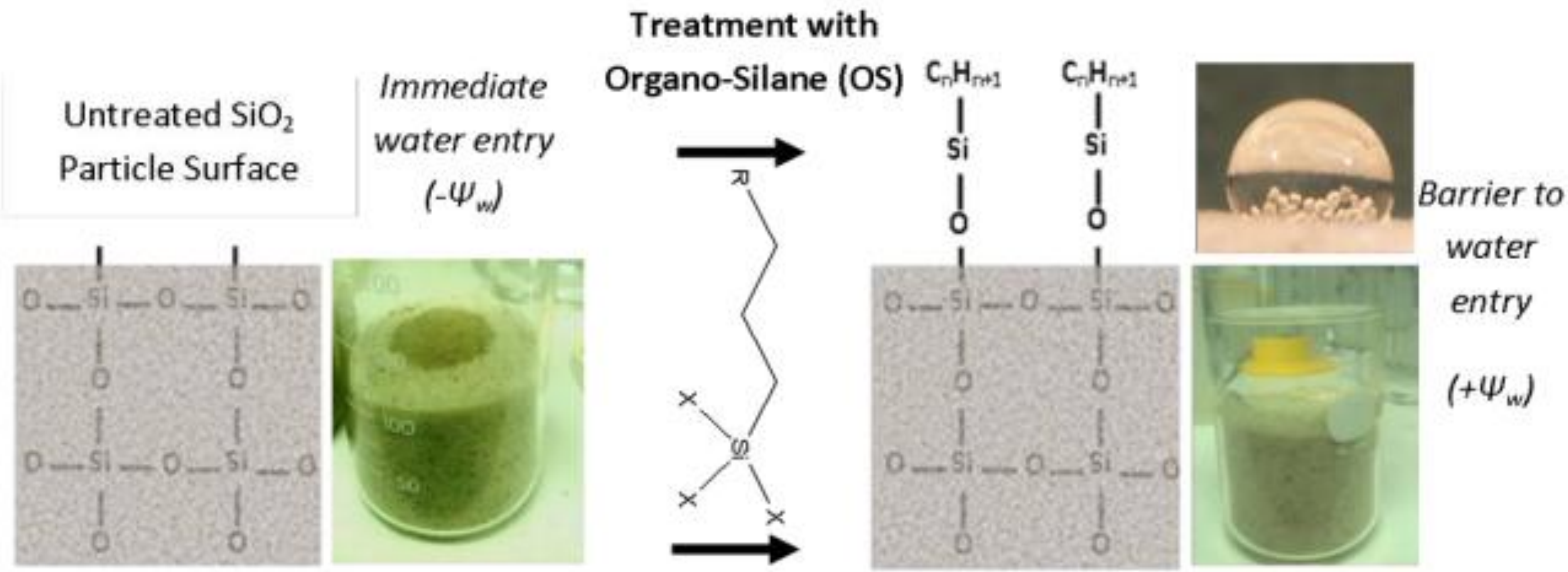
Renders surfaces water repellent (hydrophobic)



Y = "Organofunctional" group

X = "Silicon-functional" group

Organo-silanes

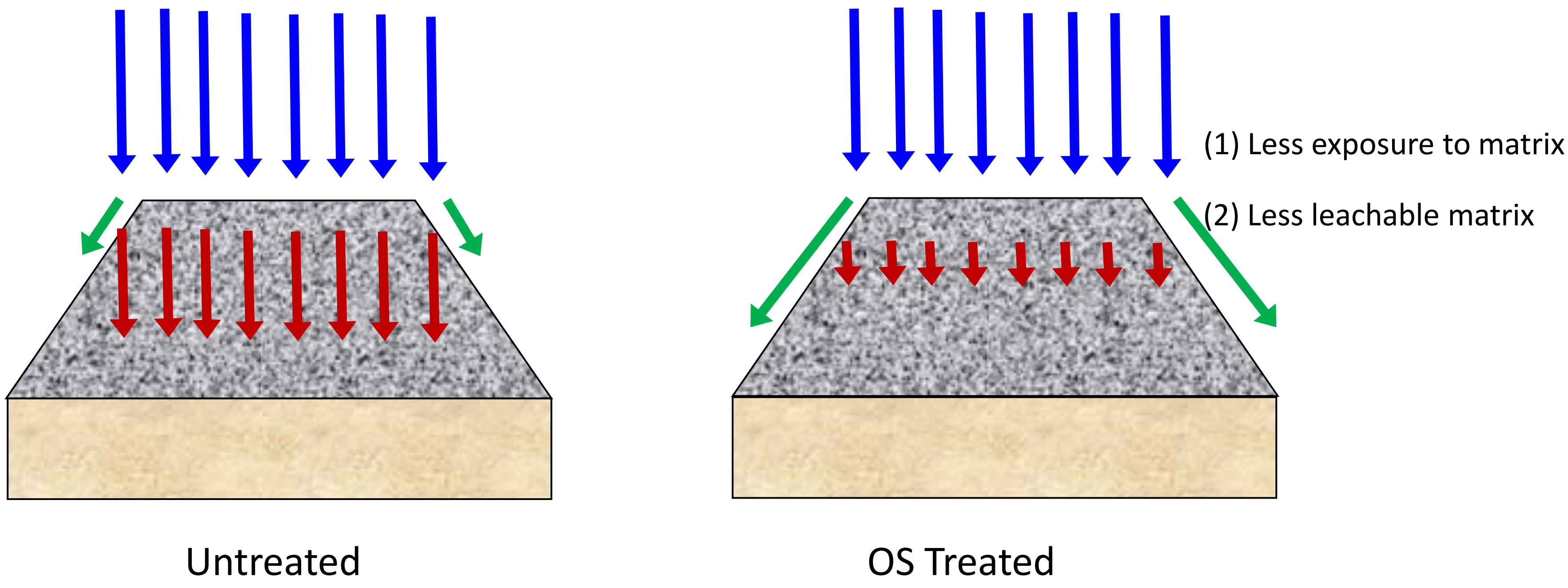


Organo-silanes

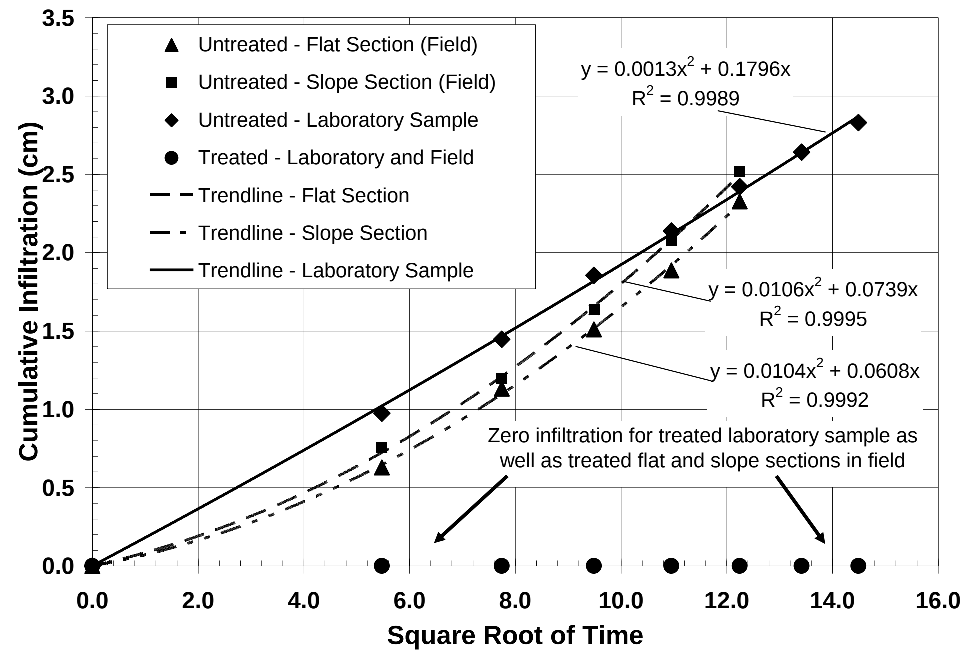
P = I + ET + RO + ΔS
P = precipitation
I = infiltration
ET = evapotranspiration
RO = runoff
ΔS = change in storage

Infiltration is a function of prevailing capillary gradient (downward)

$$Q = K \psi \left[\left(\frac{h_c - z}{z} \right) + \frac{dh}{dL} \right] A$$



Organo-silanes



Federal Register

Monday,
June 21, 2010

Part II

Environmental Protection Agency

40 CFR Parts 257, 261, 264 et al.

**Hazardous and Solid Waste Manag
System; Identification and Listing
Special Wastes; Disposal of Coal
Combustion Residuals From Electr
Utilities; Proposed Rule**

maximum dry density value.[32] This concept, it has been reported, could potentially be taken further with the use of compaction coupled with the addition of organosilanes. According to recent studies, organosilanes could take the hydraulic conductivity to zero.[33] EPA solicits comments on the effectiveness of such additives, including any analysis that would reflect long-term performance, as well as the appropriateness of a performance standard that would allow such control measures in lieu of composite liners. EPA has also observed that surface impoundments are often placed right next to surface water bodies which may present complex subsurface environments not considered by the

compactive force. The maximum dry density value (or maximum achievable dry density value) is determined by dividing the mass of the compacted material (weight divided by the gravitational force) by the volume of the compacted material.

[33] "Organo-silane Chemistry: A Water Repellant Technology for Coal Ash and Soils," John L. Daniels, Mimi S. Hourani, and Larry S. Harper, 2009 World of Coal Ash Conference. *Available at http://www.flyash.info/2009/025-daniels2009.pdf* and in the docket to this proposal.

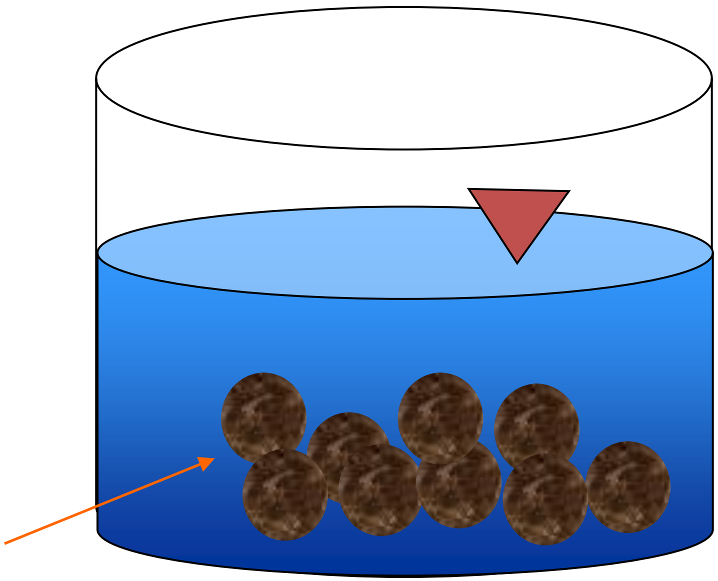
changed
and the i
have con
reduced

[34] Guidan
Coal-Fired
Institute, 19
proposal.

Evaluating Leaching Behavior

Field Reality

Lab Analogue (batch format)



Leaching constituent (e.g., soil, ash, etc.)

JD

Leachability

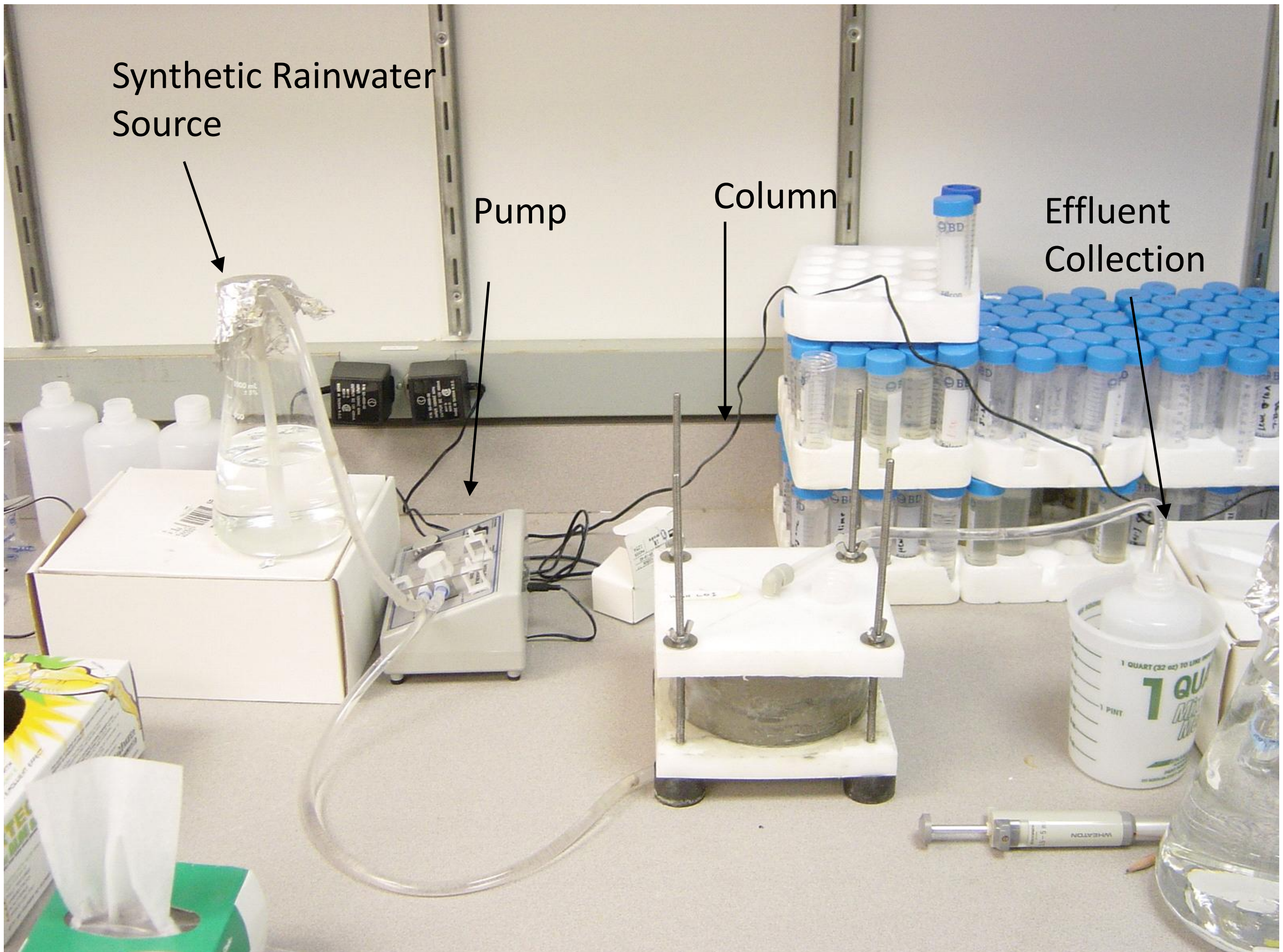
- Over sixty different leach procedures exist
- Batch (e.g., SPLP, TCLP, EP Tox) and Column testing are most common methods
- New Leaching Environmental and Assessment Framework (LEAF):

LEAF Method	Title	Output
1313	pH-dependence	Contaminant leachability at a liquid to solid ratio of 10:1 for pH values 2-13.
1314	Percolation column	Contaminant leachability as a function of column percolation, flowrate set to achieve a rate of liquid to solid ratio of 0.75/day
1315	Mass transfer rates	Contaminant mass transfer coefficients for diffusion-controlled conditions
1316	Batch liquid to solid ratio	Contaminant leachability at a liquid to solid ratio of 10, 5, 2, 1 and 0.5 at the “natural” pH of the material.

Notes: See http://devmconnors.com/leaf/downloads/test-methods/ for test methods and data templates.

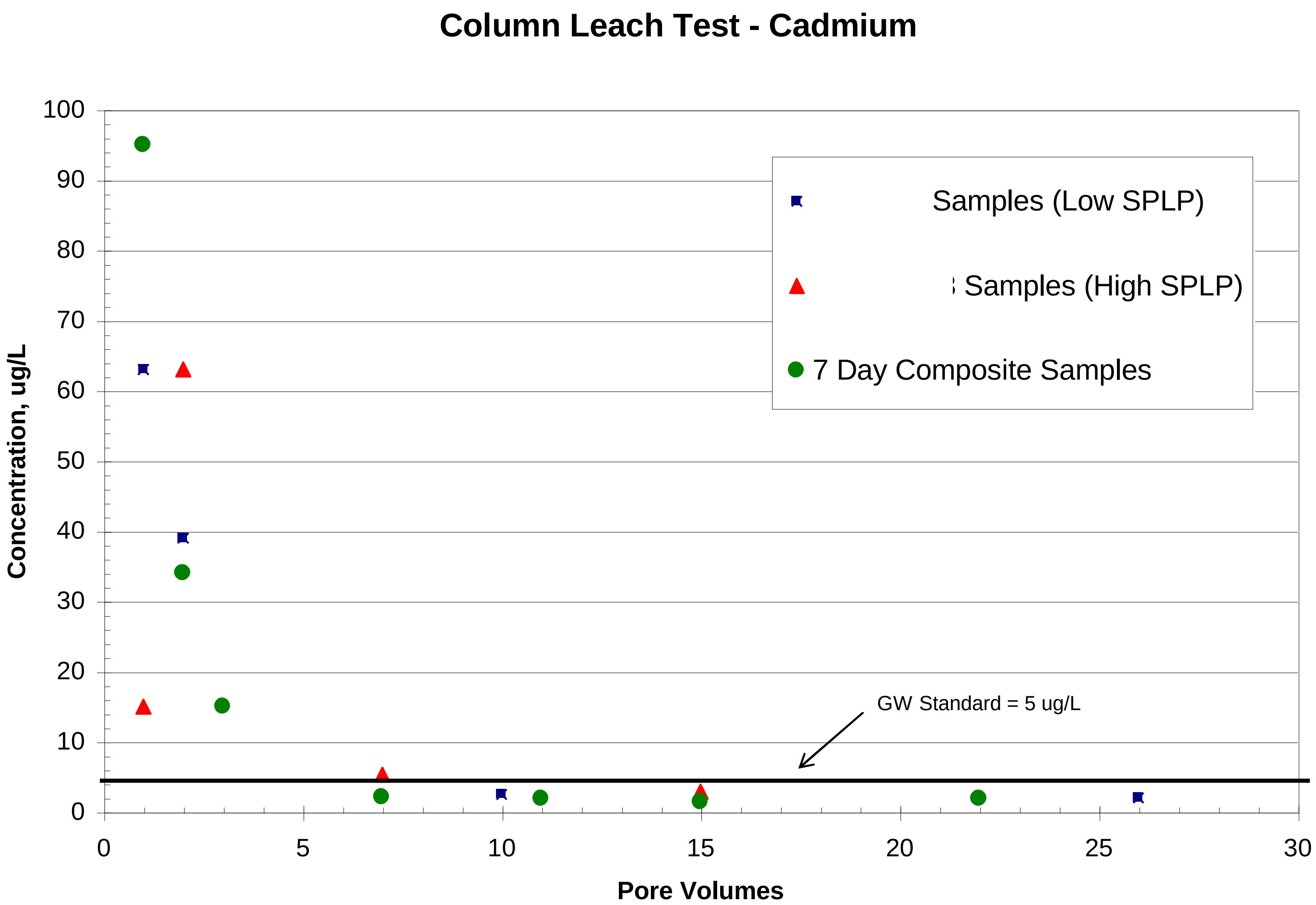
Table acquired from: Hardin, C.D. and Daniels, J.L. (2011) “Preserving Structural Fill and Mine Reclamation as Acceptable Beneficial Reuse of CCRs” World of Coal Ash Conference, Denver, CO, May 9-12, 2011

Column Leach Testing



JD

Typical Leachate Data



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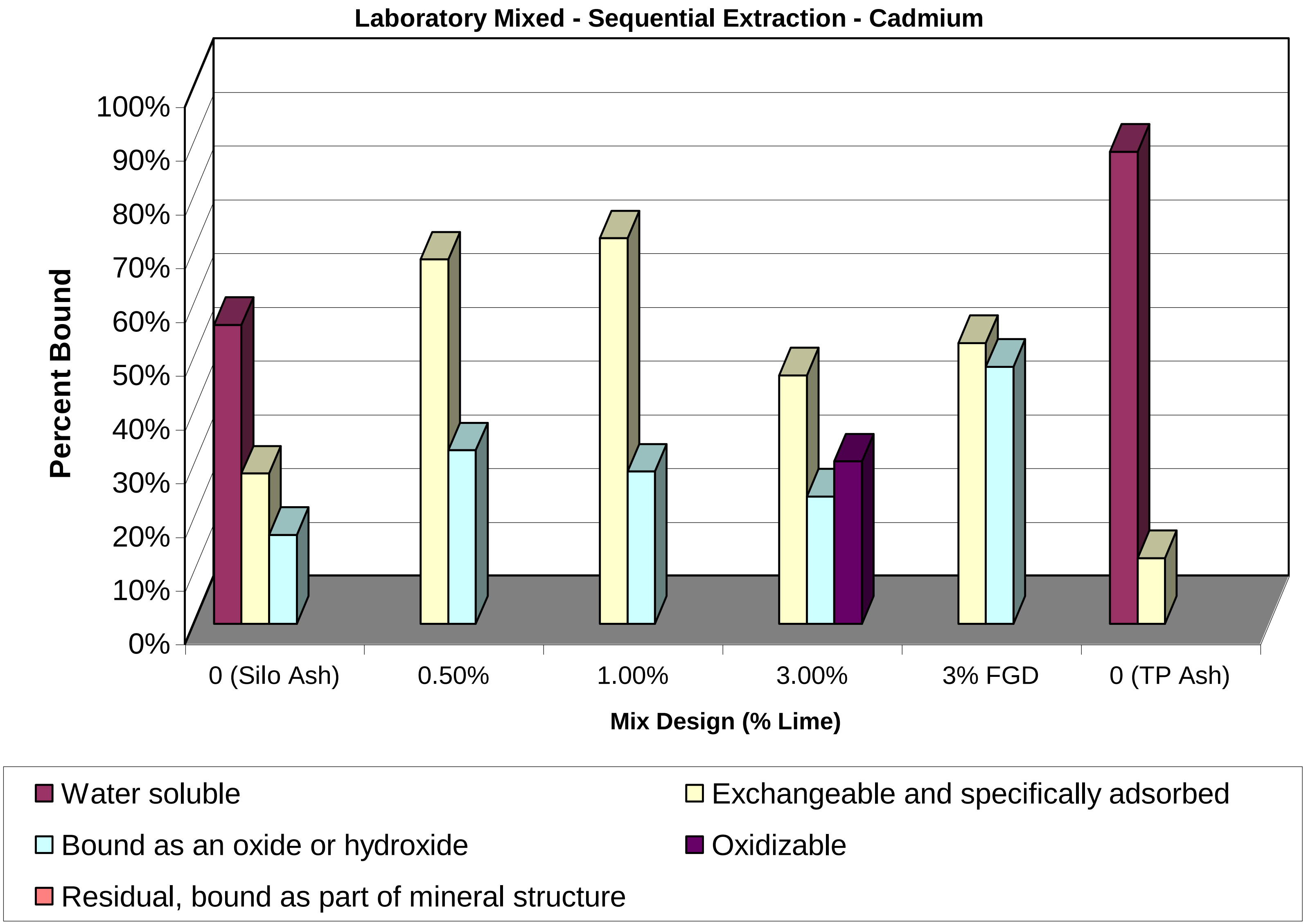
Typical Leachate Data



Parameter *(all values in mg/L, except pH)*	**Fly Ash**	**FGD gypsum (unstabilized)**	**FGD gypsum (stabilized with Poz-O-Tec®)**
pH	4-6	6-8.5	9.5-11.5
TDS	4000-6000	16,000-20,000	700-1800
SO_4^{2-}	800-1200	7000-10,000	300-850
Arsenic	0.01-0.20	≤ 0.02	0.003-0.02
Barium	< 0.50	< 0.50	< 0.50
Cadmium	< 0.01	< 0.01	< 0.01
Chloride	30-40	-	60-120
Chromium	< 0.05	< 0.05	< 0.05
Copper	2-6	-	0.10 – 0.50
Fluoride	-	-	< 1.0
Iron	80-150	-	< 0.20
Lead	0.20 – 0.50	< 0.10	< 0.05
Manganese	-	-	< 0.05
Mercury	< 0.002	< 0.001	< 0.001
Nitrate	-	-	< 0.50
Selenium	< 0.06	< 0.06	< 0.01
Silver	< 0.05	< 0.05	< 0.05
Zinc	7-9	-	< 0.10

[1]ASTM Standard Leach Test, 48 hour shake procedure

Evaluating Leaching Behavior

- Relating Leaching Data to Source Durations
  - All materials are exhaustible
  - Compare volume of precipitation in field to volume of leaching solution used in lab to make predictions of time-dependent leaching
  - Compare ratios:

    Lab Leachant Volume / Solid Mass

    Field Leachant Volume / Solid Mass

    [Field Leachant Volume = f(infiltration) = f(time)]

    Develop relationship between leached concentration in short period of time (in lab) to concentrations leached over many decades

JD

Parting Thoughts

- **Costs really depend on plant and design basis**
  - **Reduce leachability to zero?**
  - **Cover/liner type configuration?**
- **Straightforward, yet plant specific testing required**
- **Data forthcoming**