Stabilization and solidification of brine water containing selenium, chromium, copper, and mercury utilizing microwave enabled sol-gel process

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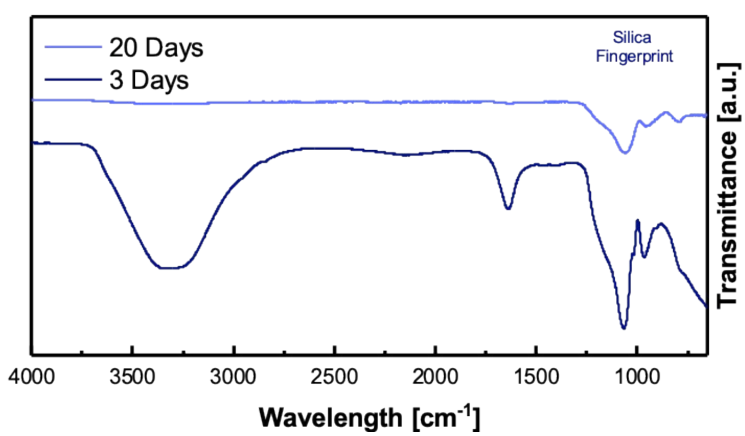
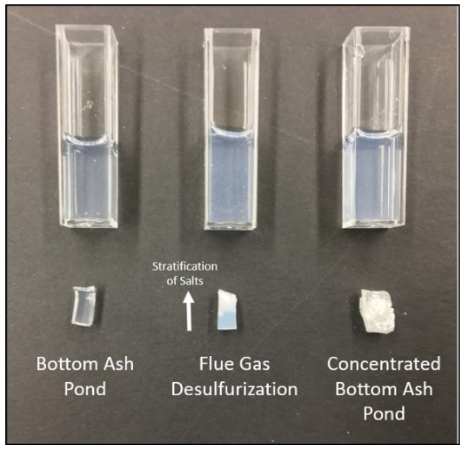
The following supporting information appendix consists of six pages, including calculations, two figures and four tables.



Supplementary Figure S1. Condensation Reaction. FT-IR Spectra of samples at 3 days (gels) and 20 days (glass).



Supplementary Figure S2. Gelation and encapsulation of three brine waters (top three) immediately after gelation and (bottom three) after 20 days of drying. The volumes of sample in the vials shown are 2 mL per vial.

Supplementary Table S1: Structural Assignments of Raman Bands during TMOS Hydrolysis

Intermediate	Raman Shift (cm^{-1})
$Si(OCH_3)_4$	646
$Si(OCH_3)_3(OH)$	673
$Si(OCH_3)_2(OH)_2$	697
$Si(OCH_3)(OH)_3$	725
$Si(OH)_4$	750

CH_3OH	1029

Supplementary Table S2: Structural Assignments of FTIR Peaks in TMOS Condensation

Peak Assignment	Band Position (cm^{-1})
H-O-H (ν_s, ν_{as})	3300
H-O-H (δ)	1638
Si-O-Si (ν_{as})	1080
Si-O-H (ν_s)	940
Si-O-Si (ν_s)	750

Supplementary Table S3: Ratios of Si-O-Si and Si-O-H bands in Encapsulated Solids

	Si-O-Si (1080 cm^{-1}) Transmittance [a.u.]	Si-O-H (940 cm^{-1}) Transmittance [a.u.]	Peak Ratio
CBAP	42.41	24.12	1.76
BAP	13.35	8.90	2.06
FGD	18.52	10.81	1.71
DI	11.25	5.66	1.99

Supplementary Information -Table 4

Calculations for TMOS and Ion concentration in our samples:

1 ml of 40% v/V TMOS solution is combined 1ml wastewater sample to make the gel

40% v/v of 1 ml TMOS solution = 0.00271 moles (Density of TMOS=1.03 g/ml and molar mass = 152 g/mol)

So, number of TMOS molecules = .00271 moles x 6.023 x 10^23= 1.63 x 10^{21} TMOS molecules.

Therefore there should be 1.63 X 10^{21} sites. (assuming 1 per molecule)

5 ppm Cu = 5 x 10^{-6} g/ml

$$\frac{(5 \text{ x } 10^{-6} \text{ g/ml x } 6.02 \text{ x } 10^{23} \text{ Cu ions/mol})}{63.5 \text{ g/mol}} = 4.7 \text{ x } 10^{16} \text{ Cu Ions}$$

Therefore, the ratio of available sites to 3 x 10^4 divided by 2 , which is 1.5 x 10^4, which is enough to capture 5 ppm or higher. However, this is not observed as we obtained 50% leaching at 5000 ppm. So we can not assume 1 site per TMOS molecule, and it should be around 10% or less of the available sites per molecule. That will put us in the ballpark of 1500 ppm, which is a reasonable number and is subsequently higher than what is observed in any of the waste water samples.

(a) In presence of divalent cation and their respective calculations:

Total ion concentration in 1 ml Flue Gas Desulfurization (FGD) wastewater sample:

8700 ppm Ca = 8 x 10^-3 g/ml

(8.7 x 10^-3 g/ml x 6.02 x 10^23 Ca ions/mol) = 1.3 x 10^20 Ca Ions

$$\overline{\hspace{10em}}$$
40 g/mol

2000 ppm Mg = 2 x 10^-3 g/ml

(2 x 10^-3 g/ml x 6.02 x 10^23 Mg ions/mol) = 5.0 x 10^19 Mg Ions

24 g/mol

The ratio of number of sites available to number of ions to capture is still 5:1 (again assuming 1 site per TMOS available, with 2 sites required per divalent cation).

Also, there is high concentration of chloride (9000 ppm) present in the wastewater. Ion pairing will occur between the Ca^{2+}/ Mg^{2+} ions and the Cl^{-} ions which will favor the heavy metal binding by making more binding sites available in the gel.