NAXOS2018

School of Environmental Science and Engineering
Guangzhou University

Utilization of Al-/Fe-/Si- Ceramic Matrices for Cadmium Detoxification in Wastes

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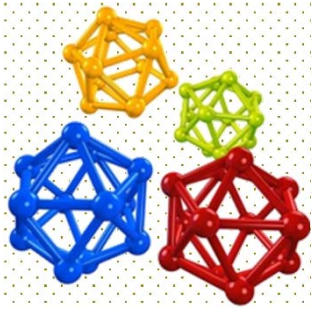


Guangzhou University (GZU)

Comprehensive

Being to be High-level

Guangdong Province

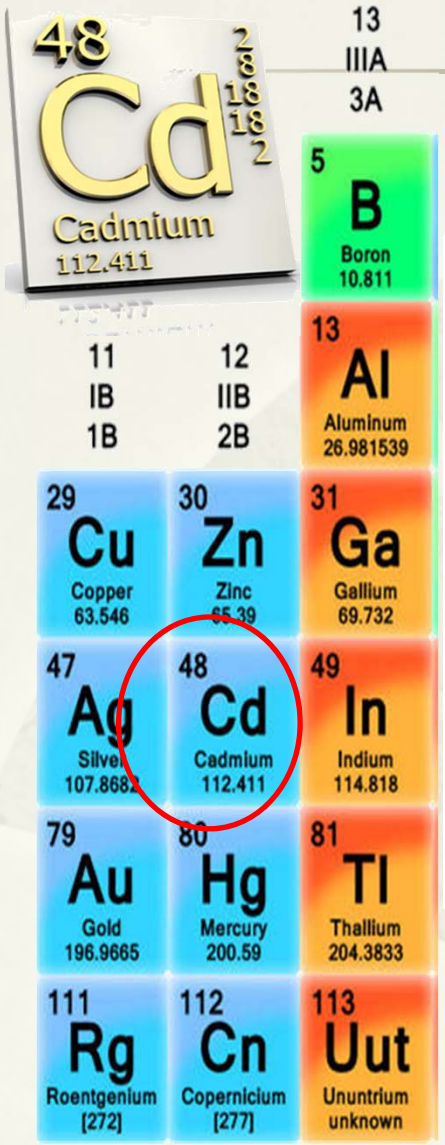
Guangzhou University (GZU)

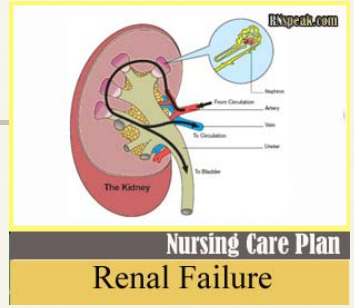
Guangzhou City

GZU h cluding philoso nomics, admini

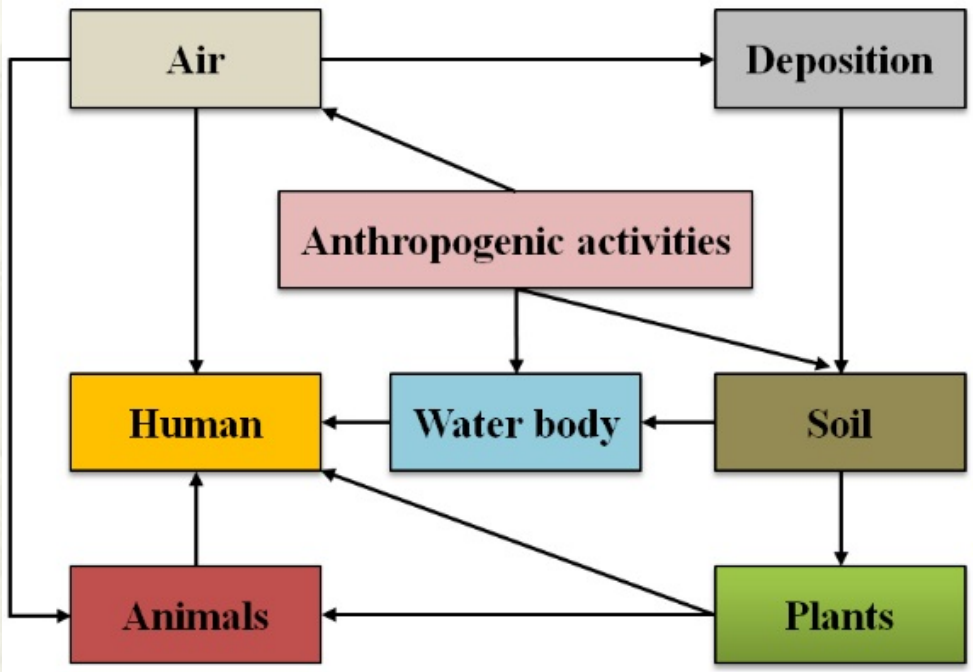
Website: http://english.gzhu.edu.cn/index.htm

Cadmium

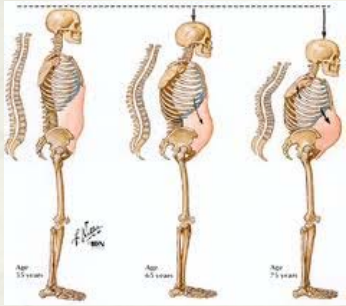




Kidney damage



Main routes for entry of cadmium into the food chain and uptake by human. (Vromman, V., et al., 2008)

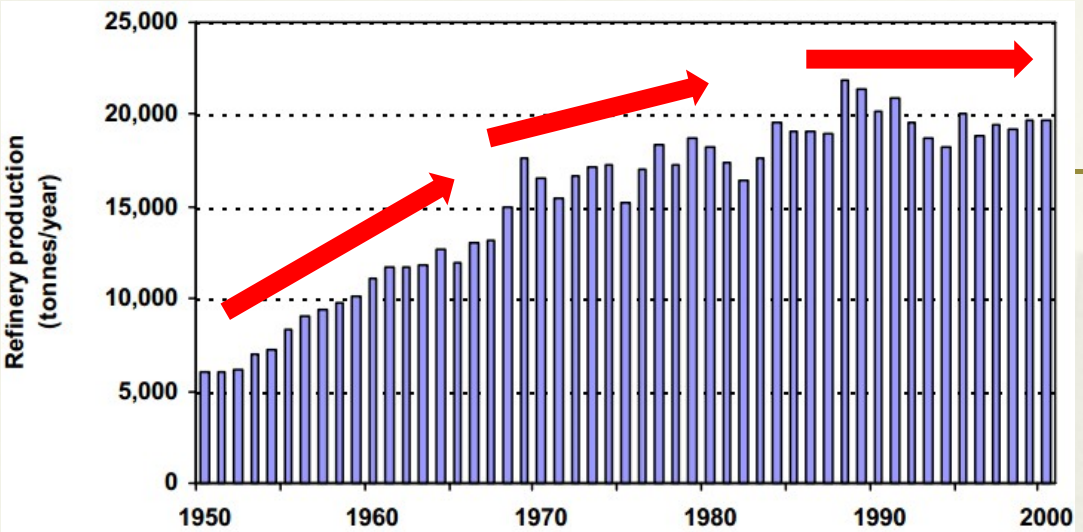


Skeleton deformation

Lung cancer

- Since 1990s, Cd was classified as a group 1 carcinogen (Program 2014)

Cadmium Production and Utilizations

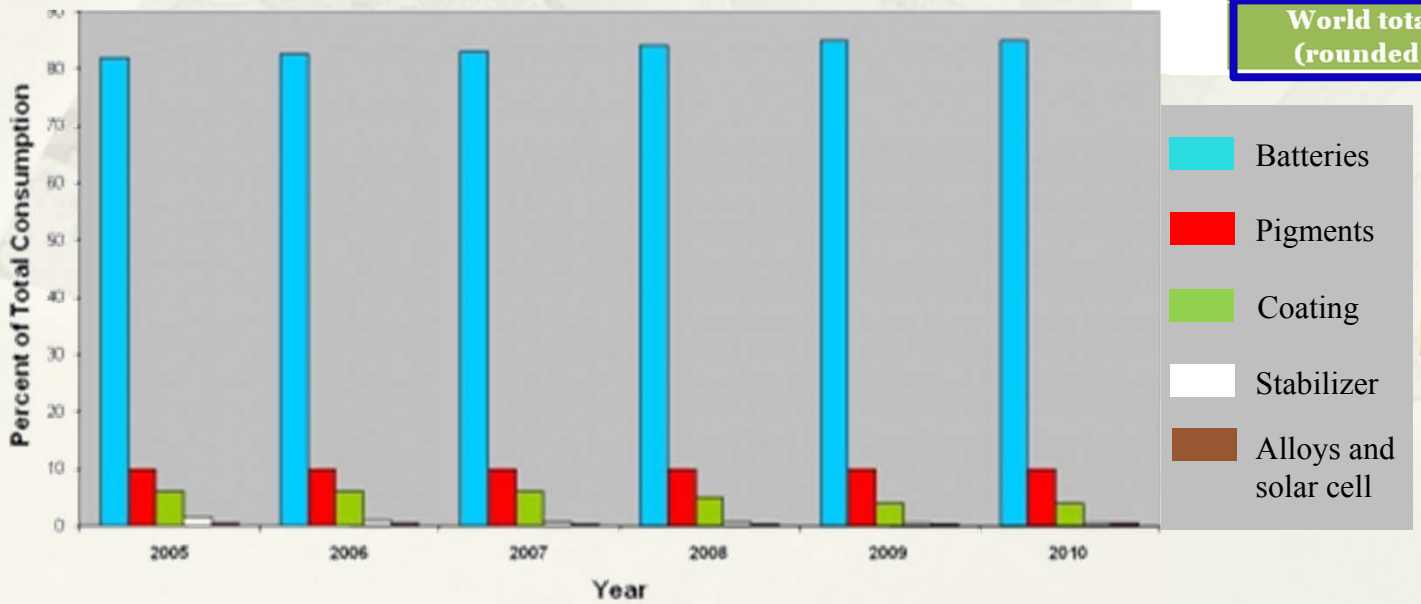


Global production of refined cadmium, 1950-2000.
(International Cadmium Association (ICdA), 2002)

World cadmium refinery production (ton)

(Data in metric tons of cadmium content unless otherwise noted --USGS,2014)

Country	2012	2013
Australia	380	380
Bulgaria	420	420
Canada	1,100	800
China	7,300	7,400
India	620	630
Japan	1,800	1,900
Kazakhstan	1,300	1,400
Korea, Republic of	3,000	3,900
Mexico	1,624	1,630
Netherlands	560	560
Peru	684	685
Poland	530	400
Russia	700	850
Other countries	880	850
World total (rounded)	20,900	21,800



Trends in Cadmium Consumption from 2005 through 2010. (ICdA, 2013)

Cadmium-Laden Sludge

Discharged

Transported

Precipitated

Production/After used **Water body** **Sediment/Sludge**

Incidentally/intentionally discharged!

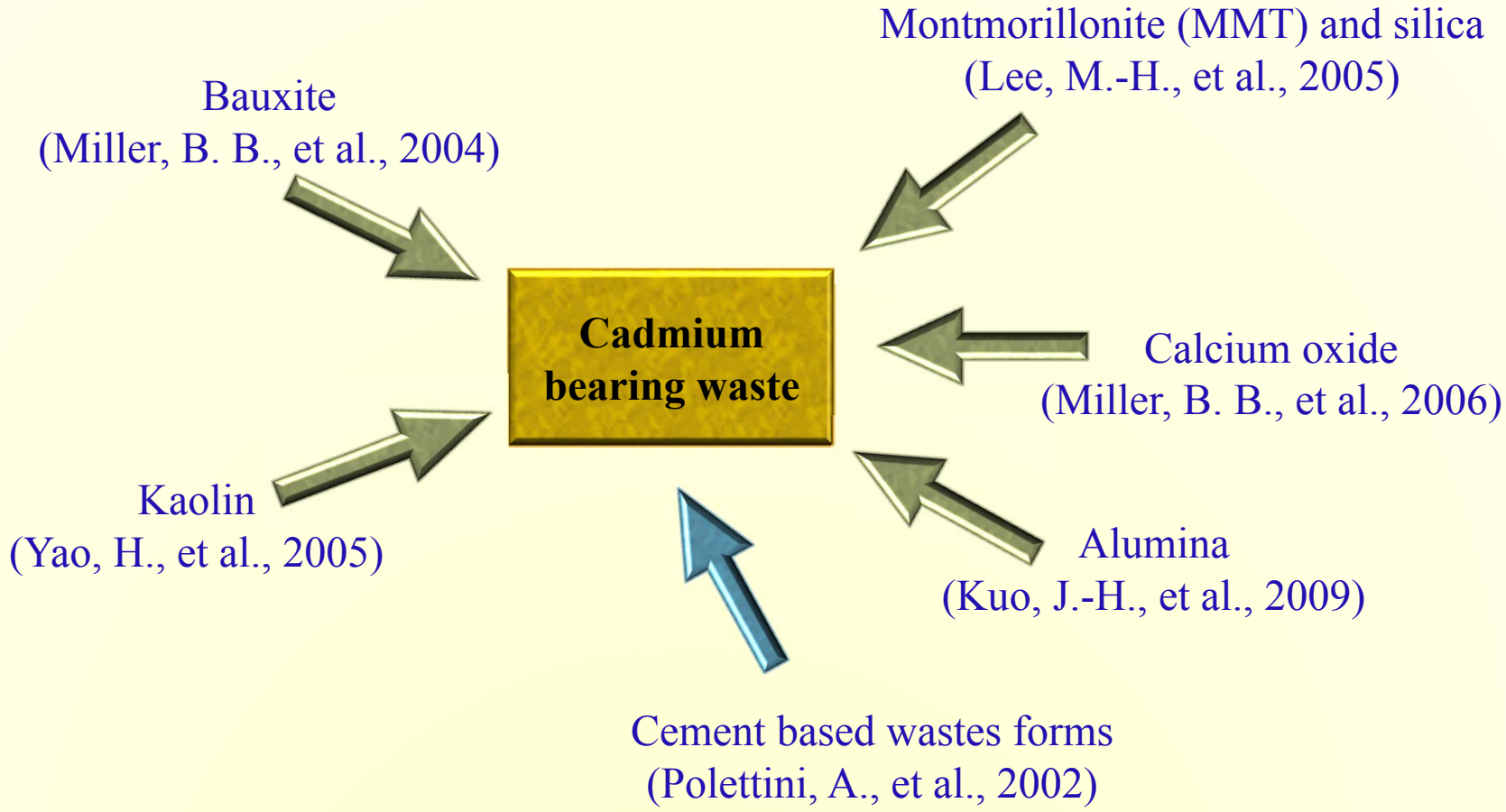
20 tons of the cadmium discharged into Liujiang river(Guangxi, China) by a Mining plant, causing severe cadmium pollution affecting up to 4 million people. (Reported in January, 2012)

Difficult to remediate!

A ￥40.7 billion project (began in 1979) to restore cadmium contaminated farmland in the Jinzu River basin, Japan. (Reported in March, 2012)

Common Treatment of Cadmium Bearing Waste

- Solidification/stabilization (S/S) process



Drawbacks:

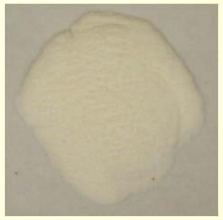
The need of additional stabilization due to the weak binding ability of sorbents by physical or chemical adsorption.

Proposed Technology for Cadmium Stabilization

Techniques — **Ceramic Sintering Process (CSP)**

- **Environmentally Friendly**
- **Waste-to-Resources**

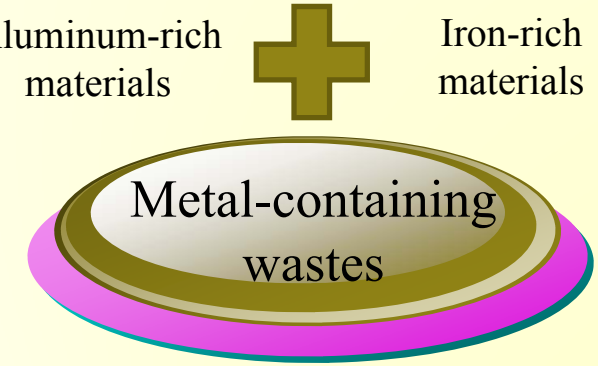
Thermally converting them into non-hazardous / less hazardous products.



Aluminum-rich materials

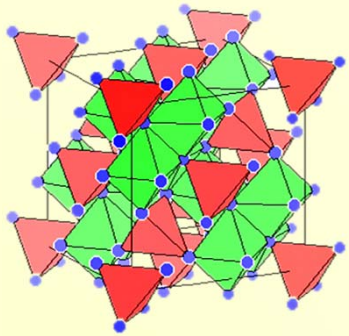
or

Iron-rich materials



Sintering

Ceramic products

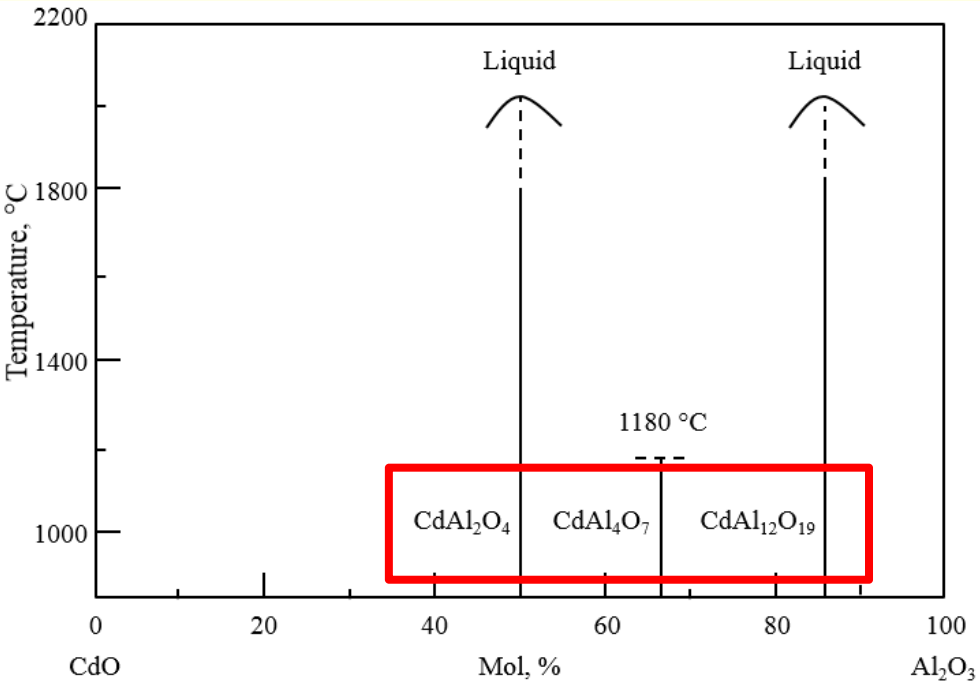


With high acidic resisting ability

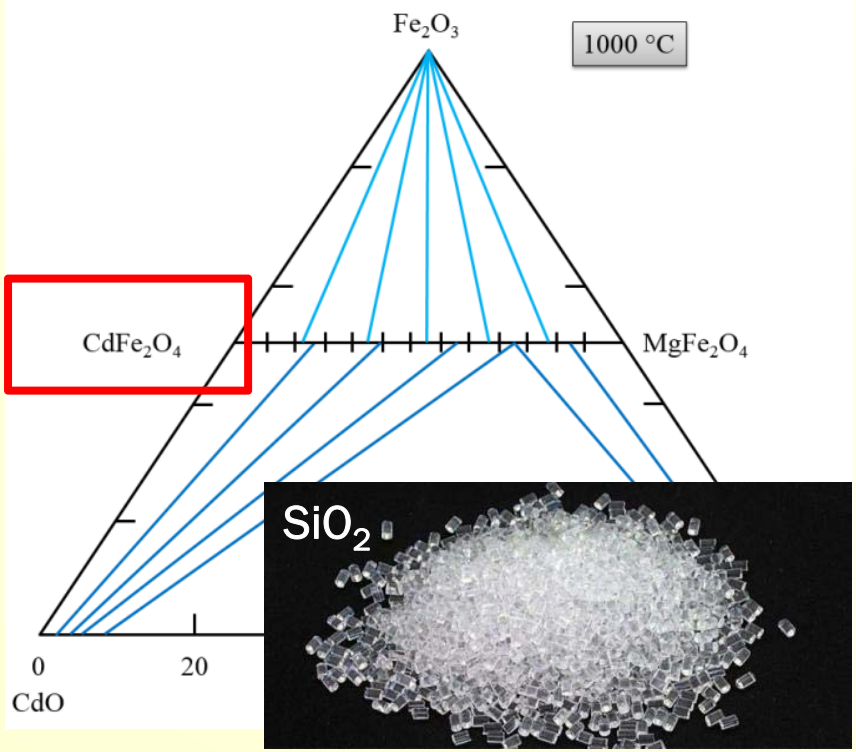
K. Shih, et al. E.S&T., 2005; Y. Tang, et al. E.S&T., 2012

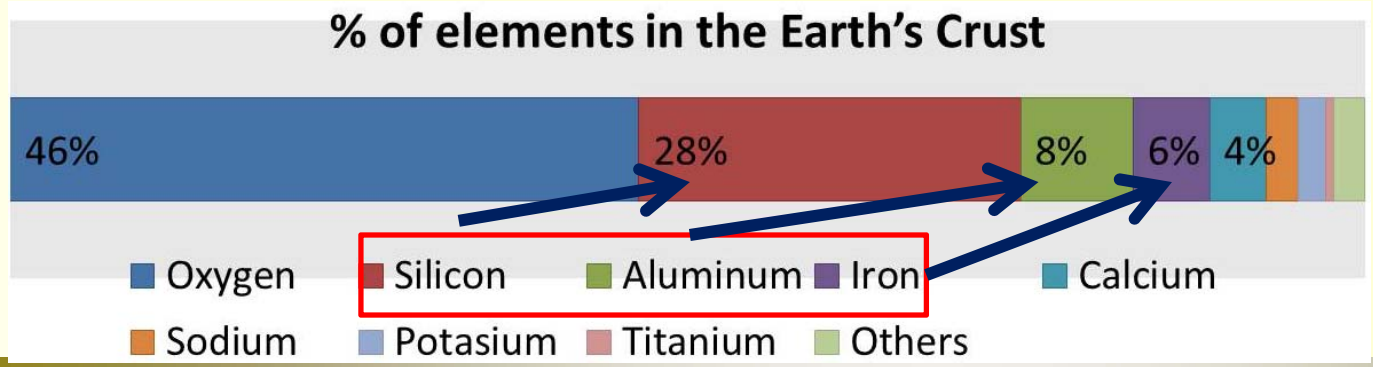
Equilibrium Diagrams of Cd-Al-O and Cd-Fe-Mg-O Systems

Cd-Al-O system (Colin, 1968)



Cd-Fe-Mg-O system (Bashkirov and Kornilova 1980)

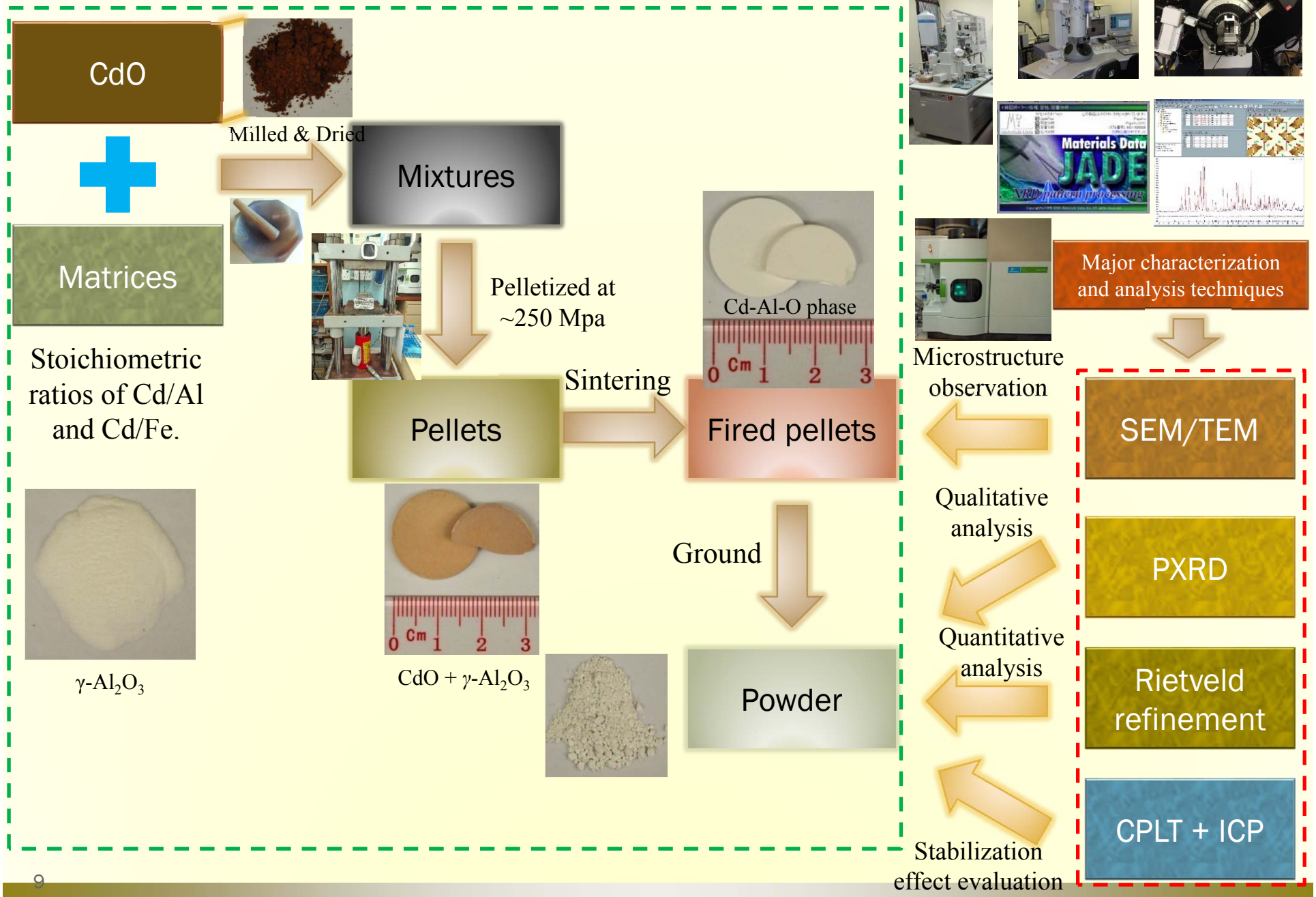




Gamma-Al_2O_3

Hematite

Sample Preparation, Characterization and Evaluation



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Quantification Quality Evaluation for QXRD analysis

"R-pattern", R_p, $R_p = \frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum Y_{o,m}}$

"R-weight pattern", R_{wp}, $R_{wp} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{w_m Y_{o,m}^{\ 2}}}$

"R-expected", R_{exp}, $R_{exp} = \sqrt{\frac{\sum M - P}{\sum w_m Y_{o,m}^{\ 2}}}$

"Goodness of fit", GOF, $GOF = \text{chi}^2 = \frac{R_{wp}}{R_{exp}} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{M - P}}$

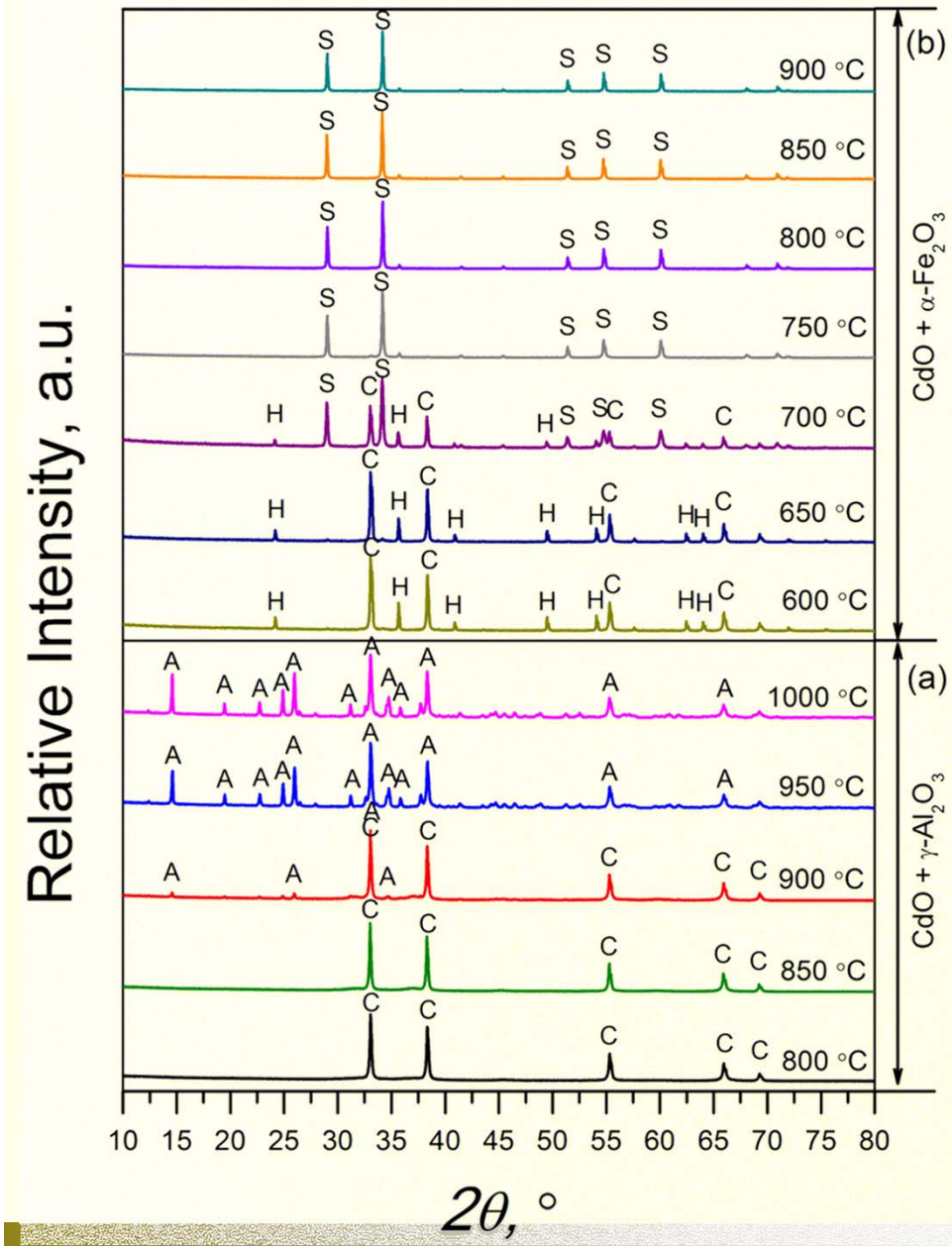
Incorporation Efficiency Evaluation

$$\text{TR}(\%) = \frac{\dfrac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}}}{\dfrac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}} + \dfrac{\text{wt.\% of CdO}}{\text{MW of CdO}}}$$

Leached Metals Normalization

$$NLCd_{SA} = 10^{-6} \times \frac{n}{k} \times \frac{C_{Cd} \times AW_{Cd}}{SW \times SA \times MW_{Phase}}$$

Cadmium-hosting Product Phase Formation via Sintering withAl-/Fe-Ceramic Matrices



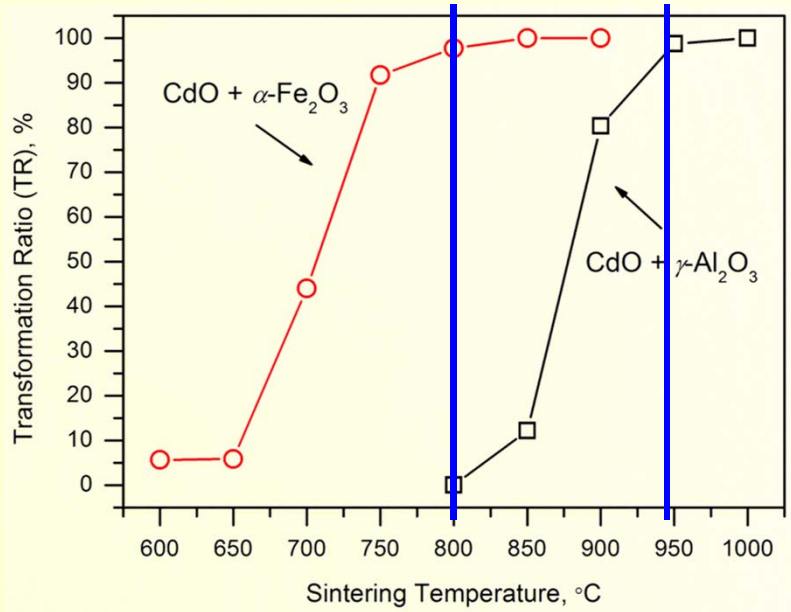
$CdO + 2\gamma\text{-}Al_2O_3 \rightarrow CdAl_4O_7$ (Monoclinic structure)

$CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$ (Spinel)

Incorporation Efficiency

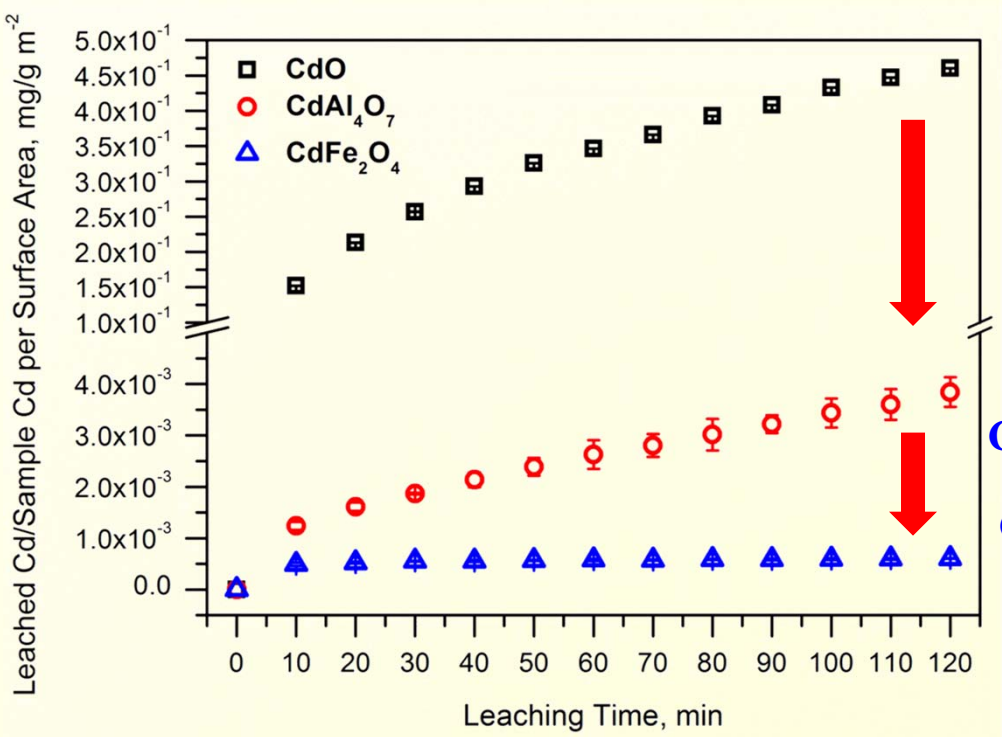
Transformation ratios

$$TR(\%) = \frac{\dfrac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}}}{\dfrac{\text{wt.\% of Aluminate or Ferrite}}{\text{MW of Aluminate or Ferrite}} + \dfrac{\text{wt.\% of CdO}}{\text{MW of CdO}}}$$



The transformation ratios (TR, %) for cadmium incorporation into $CdAl_4O_7$ monoclinic structure and $CdFe_2O_4$ spinel.

Leachability of $CdAl_4O_7$ and $CdFe_2O_4$



Leached at constant pH 4.0.

Formation of robust crystalline structures

$CdO + 2\gamma\text{-}Al_2O_3 \rightarrow CdAl_4O_7$ (Monoclinic structure)

$CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$ (Spinel)

Detoxification of the hazardous wastes

$$CdO_{(s)} + 2H^+_{(eq)} \rightarrow Cd^{2+}_{(eq)} + H_2O$$

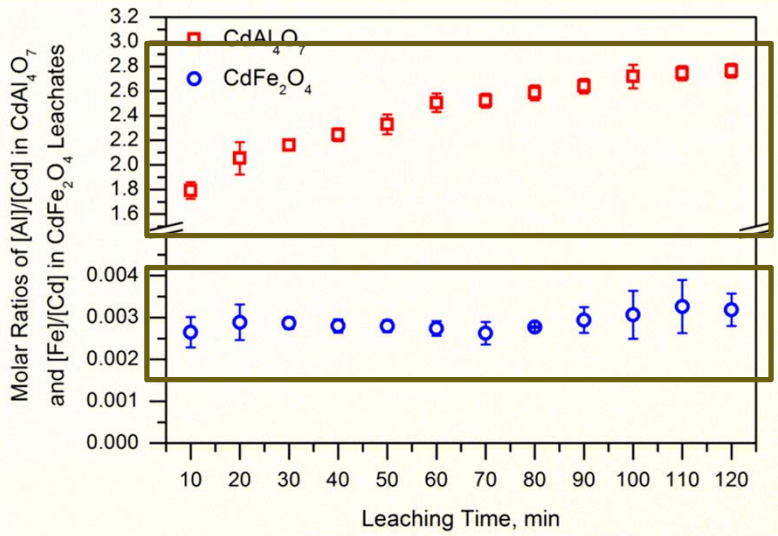
$$CdAl_4O_{7(s)} + 14H^+_{(eq)} \rightarrow Cd^{2+}_{(eq)} + 4Al^{3+}_{(eq)} + 7H_2O$$

$$CdFe_2O_{4(s)} + 8H^+_{(eq)} \rightarrow Cd^{2+}_{(eq)} + 2Fe^{3+}_{(eq)} + 4H_2O$$

$[Al^{3+}_{(eq)}]/[Cd^{2+}_{(eq)}]$ molar ratio of 4.0

$[Fe^{3+}_{(eq)}]/[Cd^{2+}_{(eq)}]$ molar ratio of 2.0

Leaching Behavior of $CdAl_4O_7$ and $CdFe_2O_4$



< 4.0

<< 2.0

$$am \cdot Al(OH)_{3(s)} \leftrightarrow Al^{3+}_{(aq)} + 3OH^{-}_{(aq)}$$

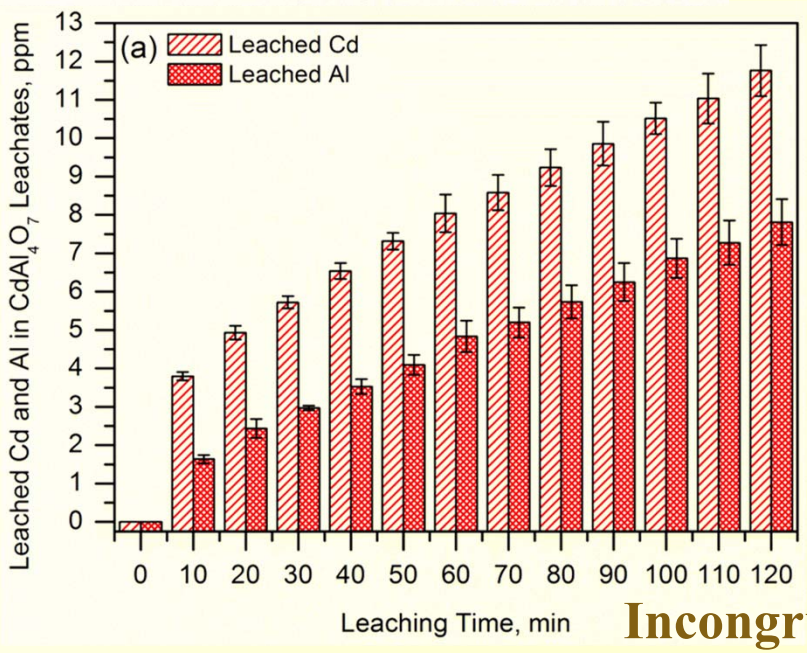
$$am \cdot Fe(OH)_{3(s)} \leftrightarrow Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)}$$

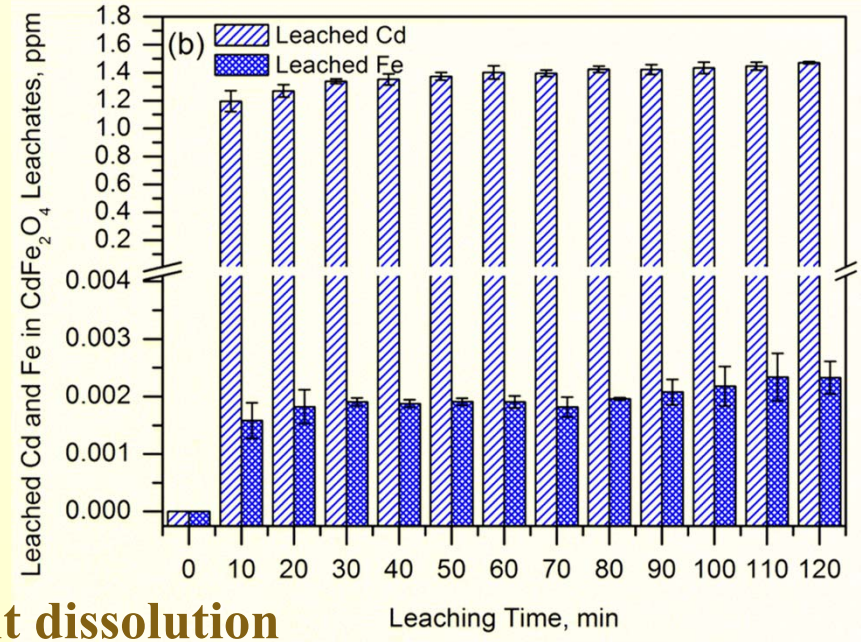
At pH 4.0

$[Al^{3+}_{(eq)}]$ should be 6.3×10^{-2} M (1701 mg/L),

$[Fe^{3+}_{(eq)}]$ should be 1.05×10^{-5} M (0.59 mg/L),

The [Al]/[Cd] molar ratios in $CdAl_4O_7$ leachates and [Fe]/[Cd] molar ratios in $CdFe_2O_4$ leachates.

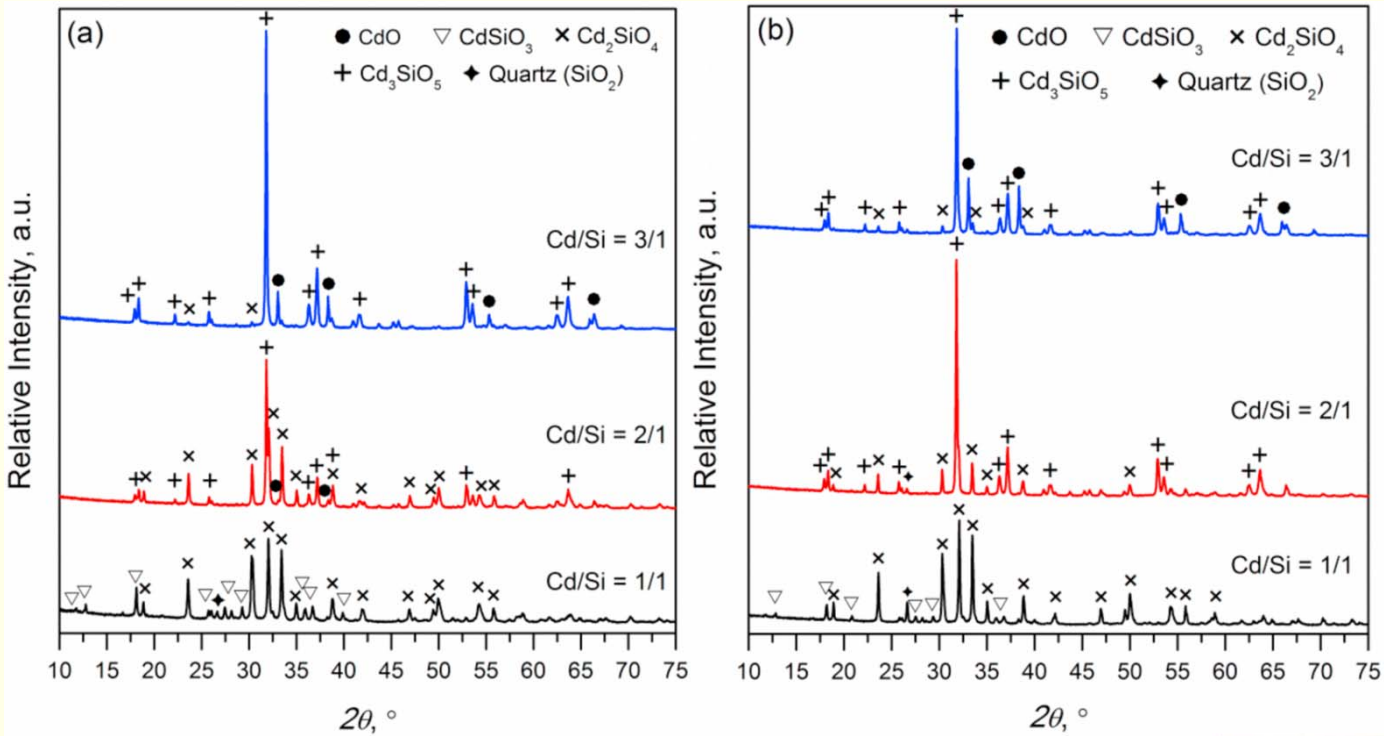




Incongruent dissolution

The (a) soluble Cd and Al concentrations in the leachates of $CdAl_4O_7$ monoclinic structure and (b) the soluble Cd and Fe concentrations in the leachates of $CdFe_2O_4$ spinel.

Cadmium-hosting Product Phase Formation via Sintering with Si-rich Ceramic Matrices

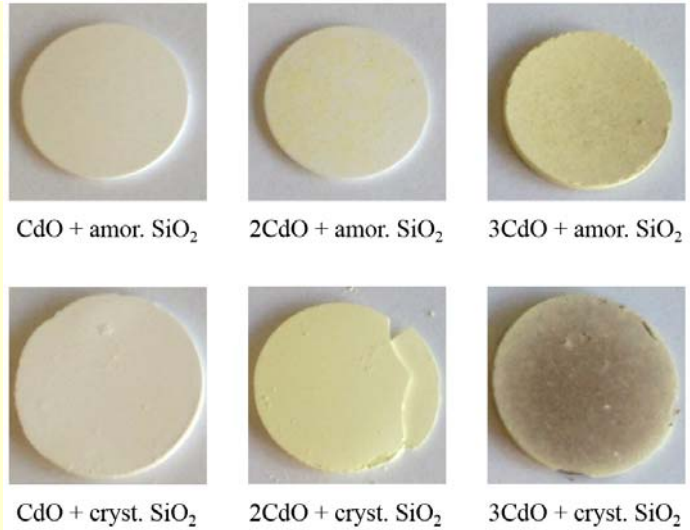


$CdO + SiO_2 \rightarrow CdSiO_3$

$2CdO + SiO_2 \rightarrow Cd_2SiO_4$

$3CdO + SiO_2 \rightarrow Cd_3SiO_5$

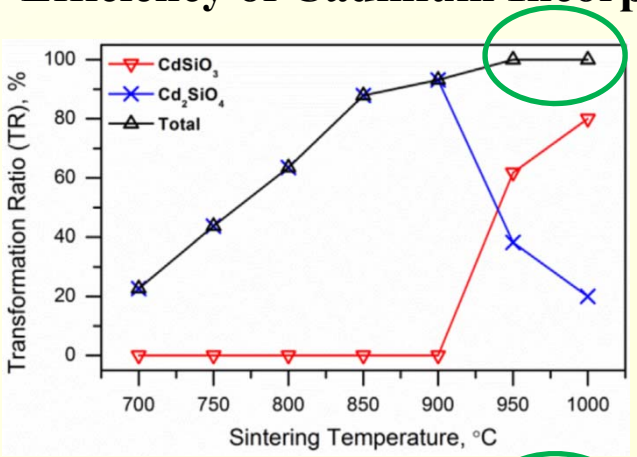
XRD patterns of sintered (a) CdO + silica fume and (b) CdO + a-quartz samples with various Cd/Si molar ratios (Cd/Si molar ratio = 1.0, 2.0, and 3.0) at 950 ºC for 3 h.



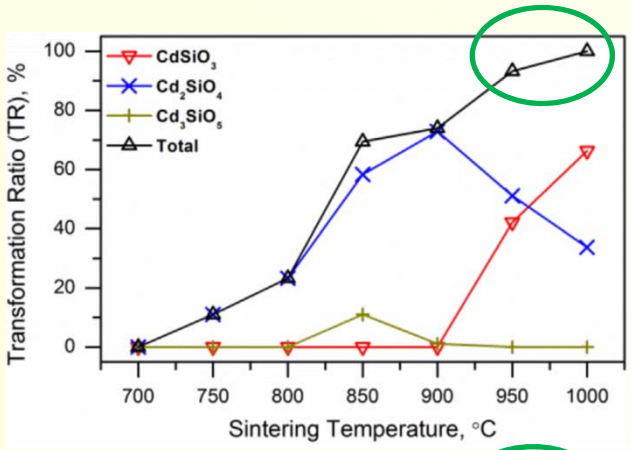
Views of sintered CdO + silica fume and CdO + α-quartz samples with Cd/Si molar ratios (Γ = 1.0, 2.0, and 3.0) at 950 ° C for 3 h.

Efficiency of Cadmium Incorporation into Cadmium Silicates

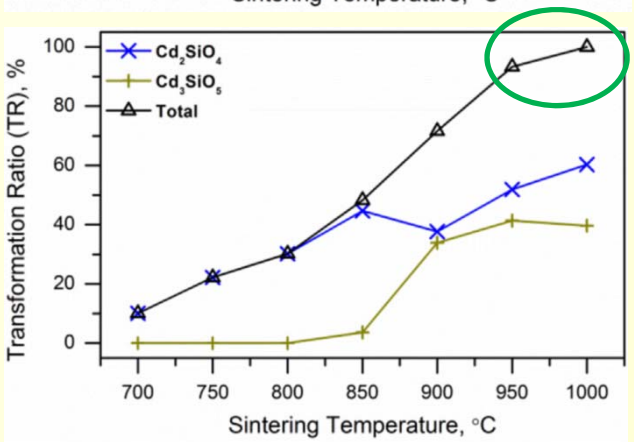
With silica fume
Cd/Si = 1.0



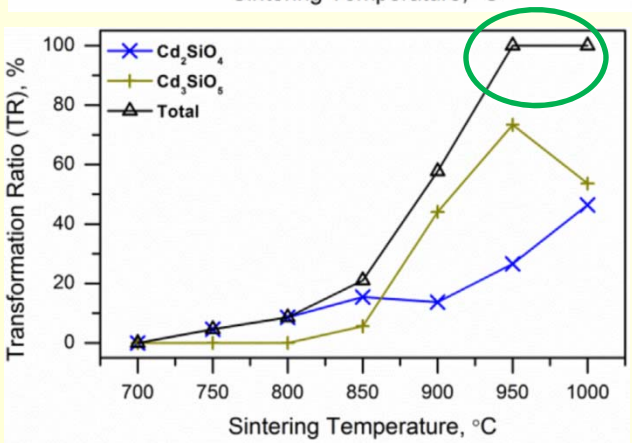
With quartz
Cd/Si = 1.0



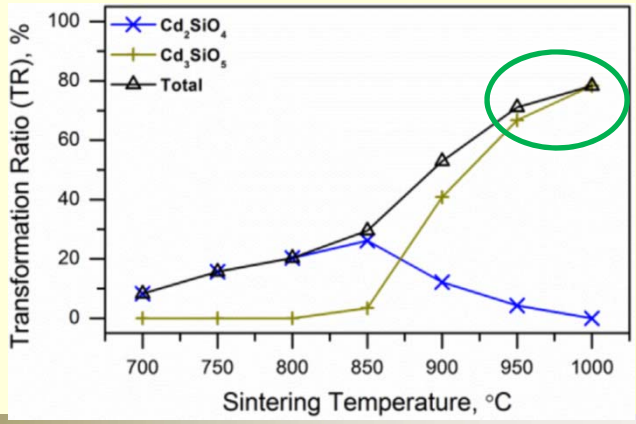
With silica fume
Cd/Si = 2.0



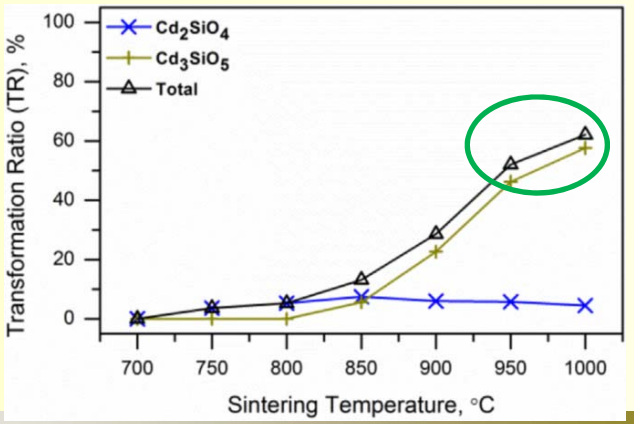
With quartz
Cd/Si = 2.0



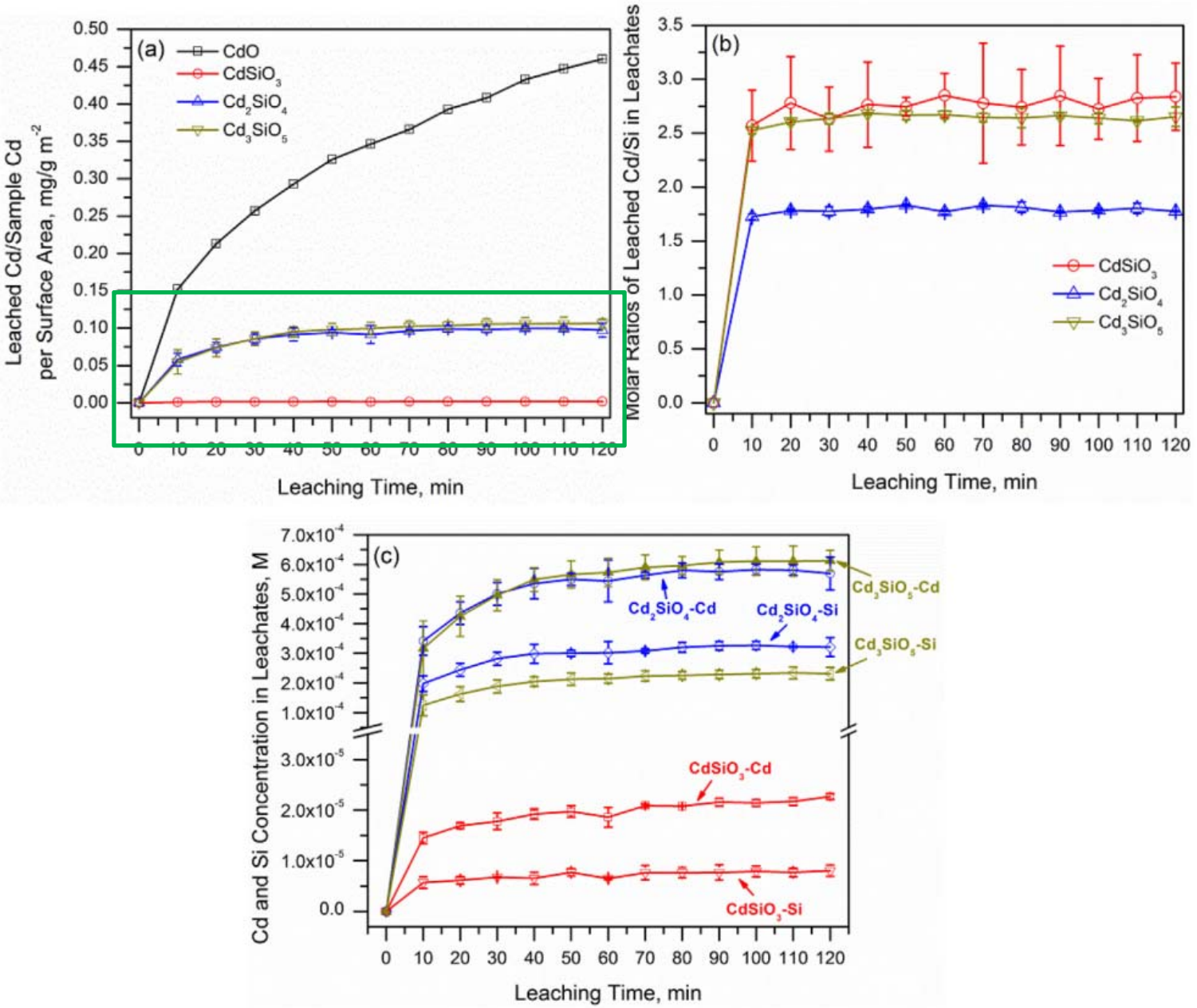
With silica fume
Cd/Si = 3.0



With quartz
Cd/Si = 3.0



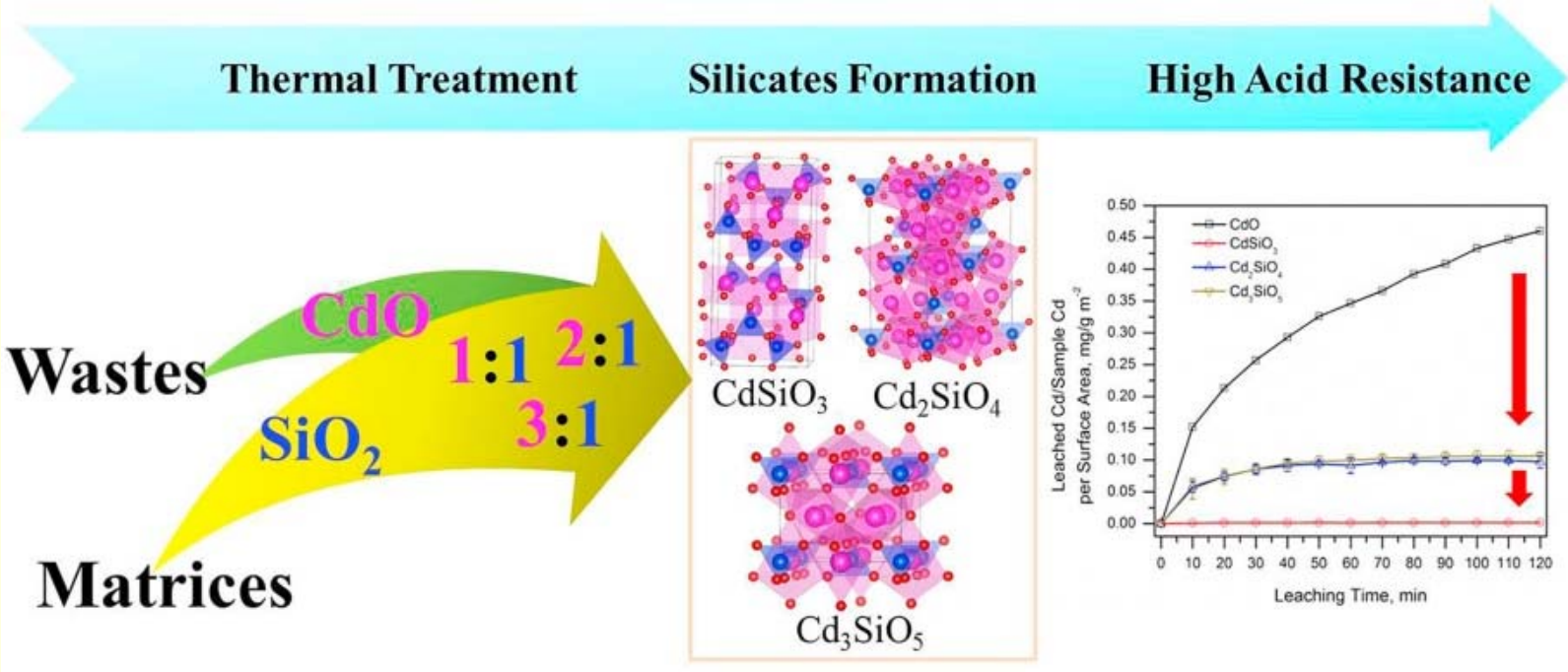
Leachability of CdO, $CdSiO_3$, Cd_2SiO_4 and Cd_3SiO_5



Summary

$CdO + 2\gamma\text{-}Al_2O_3 \rightarrow CdAl_4O_7$ (Monoclinic structure)

$CdO + \alpha\text{-}Fe_2O_3 \rightarrow CdFe_2O_4$ (Spinel)



Su et al., EP, 2018

A successful reduction of cadmium under acidic environments, identifying a promising and safe avenue for cadmium-laden sludge treatment.

Recent Publications

1. **Su, M.H.**, Liao, C.Z., Chan, T.-S., Shih, K., Xiao, T.F., Chen, D.Y., Kong, L.J.; Song, G. Incorporation of Cadmium and Nickel into Ferrite Spinel Solid Solution: XRD and EXAFS Study. *Environmental Science & Technology*, 2018, 52, 775-782.
2. **Su, M.H.,** Liao, C.Z., Chuang, K.H., Wey, M.Y., Shih K.* Cadmium Stabilization Efficiency and Leachability by $CdAl_4O_7$Monoclinic Structure. *Environmental Science & Technology*, 2015, 49, 14452-14459.
3. **Su, M.H.,** Tang, J., Liao, C.Z., Kong, L.∗, Xiao, T., Shih, K., Song, G., Chen, D.∗, Zhang, H. Cadmium Stabilization via Silicates Formation: Efficiency, Reaction Routes and Leaching Behavior of Products. *Environmental Pollution*, 2018, 239, 571-578.
Environmental Pollution, 2018, 239, 571-578.
4. **Su, M.H.**, Liao, C. Z. Lee, P.-H., Li, H.L., Shih K.* Formation and Leaching Behavior of Ferrite Spinel for Cadmium Stabilization. *Chemical Engineering Science*, 2017,158, 2017, 287-293.
5. **Su M.H.*,**Kong, L.-J. Shih, K. Stabilizing Cadmium into Aluminate and Ferrite Structures: Effectiveness and Leaching Behavior. *Journal of Environmental Management,* 2017, 187, 340-346.

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Dr. L.J. Kong

Thanks !

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