Scrubbing Wastes via Coal Fly Ash and Incorporation of the Product in Concrete for Civil Engineering Purposes

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Coal Consumption and Ash Production in Israel – 2013

Electrical Power (~6,000Mwatts)

- 4 Power Plants
- 13 Million Tons Bituminous Coal/year
- 1.3 Million Tons of Class F Fly Ash (FA)
- Sources (**South Africa**, Colombia, Indonesia, USA and Australia)

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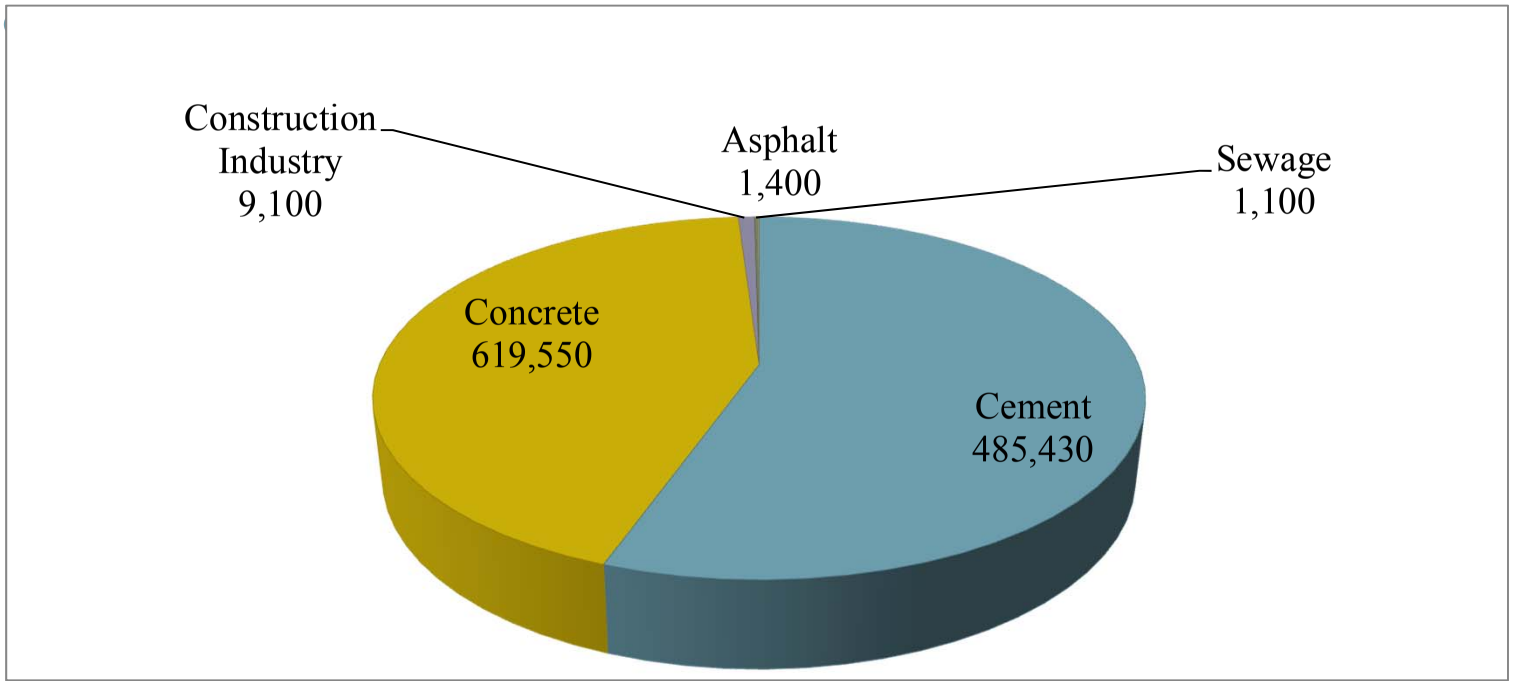
FA utilization and Disposal (worldwide)

- **Cement additive** (10%w)
- Aggregates for roads
- Marine structures
- Bricks
- Basement materials
- Reclamation
- Chemicals

FA Utilization in Israel in 2013 (100%)

- Cement Additive (10w%)
- Concrete Production
  - Construction Industry (Basements, Fillers, etc.)



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FA as a Chemical Reagent

- Source for chemicals (e.g. SiO_2, Ti, Zeolites)
- Water treatment (cleaning from trace elements
- Fixation of radionuclides?

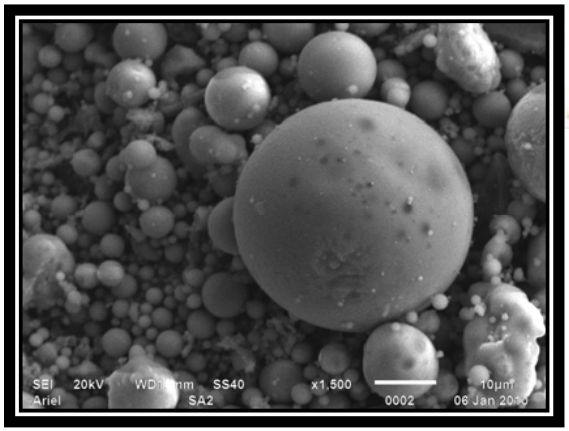
FA Properties

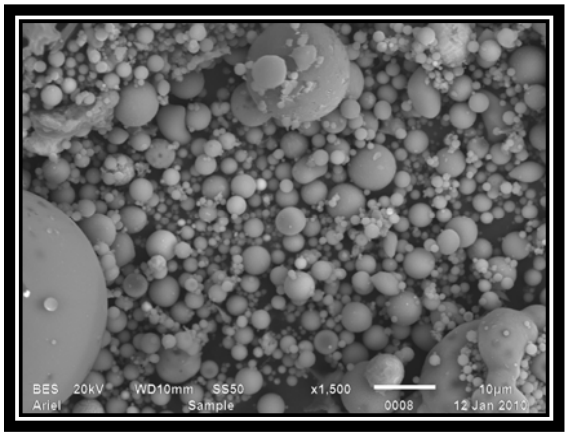
Small particles – 3-17 μm

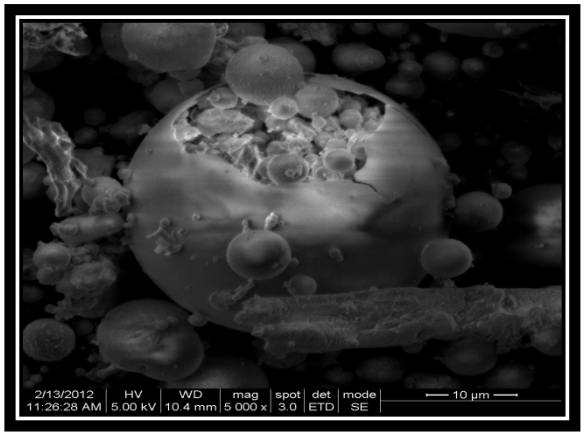
Large surface area (2-6.8x10^3 cm^2/gr)

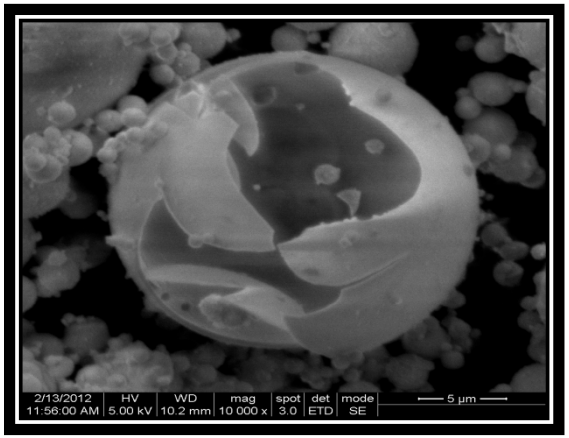
Strong interactions in aqueous solution:

- Cations
- Coordination bonding
- Precipitates



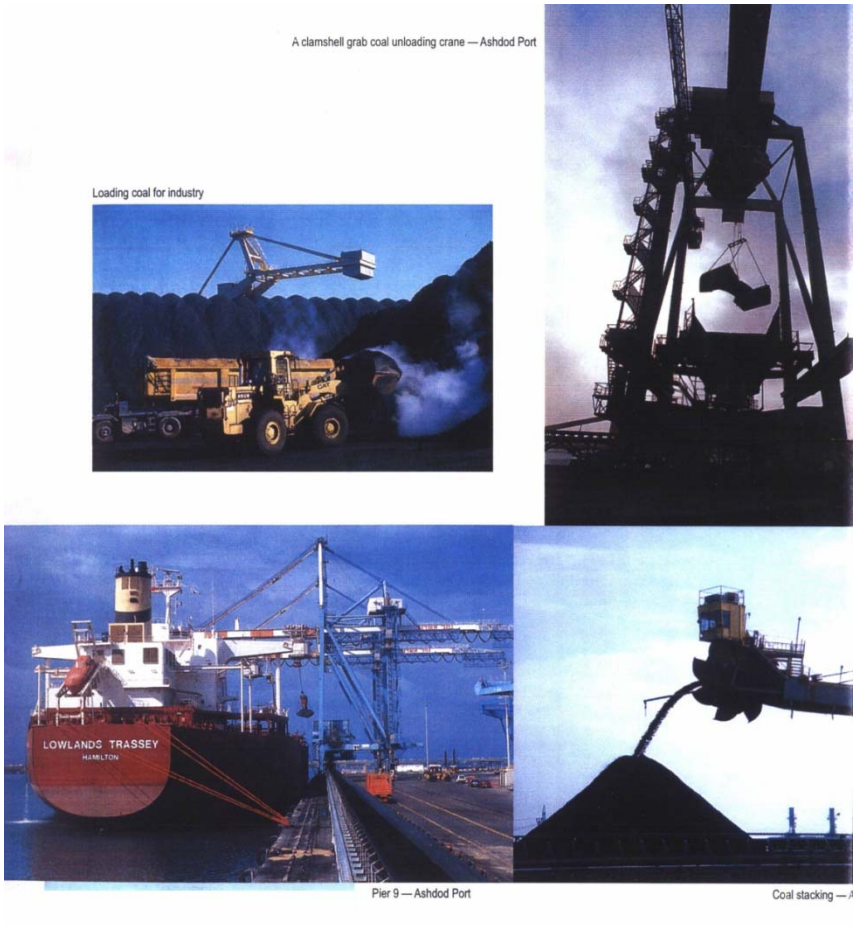






Coal and Ash Storage

Ashklon Utility



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FA in Israel is Class F (highly basic)

- Produced from low S coal combustion
- High CaO content (up to 10%)
- [Ca+K+Na+Mg]>>[S+P]
- Water/FA 10/1 (resulting pH>12.5)

Conclusion: FA good scrubber for acidic wastes

Potential scrubber for Trace Elements

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Types of FA used in Study

- South African Flyash (SAFA)
- Colombian Flyash (CO)

~70% of the ash produced in Israel

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FA Contents

Major Components (w%)

Element	SA	CO
SiO_2	42.8	54.4
Al_2O_3	31.4	20.8
TiO_2	1.75	1.05
Fe_2O_3	3.05	6.18
CaO	9.91	4.65
MgO	2.45	2.05
K_2O	0.05	0.12
Na_2O	0.02	0.05
P_2O_5	1.95	0.75
C	4-5	7-9
SO_3	0.35	0.13

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FA Contents

Minor Components (ppm)

Element	SA	CO
Ag	13.6	42.8
As	<1	31.4
Ba	2,350	1.75
Be	9.43	3.05
Cd	<2	8.35
Co	40	2.45
Cr	150	0.05
Cu	77	0.02
Mn	360	1.95
Ni	68	4-5
Pb	73	0.35

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Major Acidic Wastes in Israel

- **Phosphate Industry**

  HCl/H_2SO_4 + Phosphate Rock

- **"Motor Oil Regeneration"**

  Oleum (30%SO_3 in H_2SO_4) + Used Motor Oil

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Phosphate Industry Waste

Liquid aqueous solutions (*Haifa Chemicals South*- HCl):

pH~0-1 (0.1-1M HCl); ~0.1% Organics; 0.1-0.2% Precipitates

Solution content:

~1% PO_4^{3-} ; ~0.4% Si ; ~0.1-1M Cl

100-1,000 ppm: Fe, B, Sr, Ba, Mg, Zn, Na, K

sub-few ppm : Ag, As, Be, Cd, Co, Cr, Cu, Mn, Ni, Se, Sn, U, Ti, Tl, V

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Motor Oil Regeneration Waste

Black Organic Sludge (*Paz Shmanim Co.*):

pH~-1.2 (19M H^+)

Density ~1.6 gr/cc; Viscosity 6.2 centiStokes

4-5% H; ~17% C; ~27% (-SO_3H)

Sludge Content:

100-1,000 ppm: Fe, B, Si, Ca, Mg
5-40 ppm : Al, Cr, Na, K, Ni, Cu, Tl, Mn, Zn
0.1-4ppm : P, Ag, As, La, Se, Mo, Pb, Sr, Sn, Ti, V

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Present Treatments in Israel

- **Phosphate Industry Wastes**

  Mixing with lime (CaO) or $CaCO_3$ in large settling ponds (mainly Rotem Ampert- H_2SO_4

  in bottom of ponds Gypsum ($CaSO_4$)

  After pond is filled a layer of sand to cover

- **Motor Oil Regeneration Sludge**

  Transport of sludge to Central Hazardous

  Treatment Facility (storage in Ponds)

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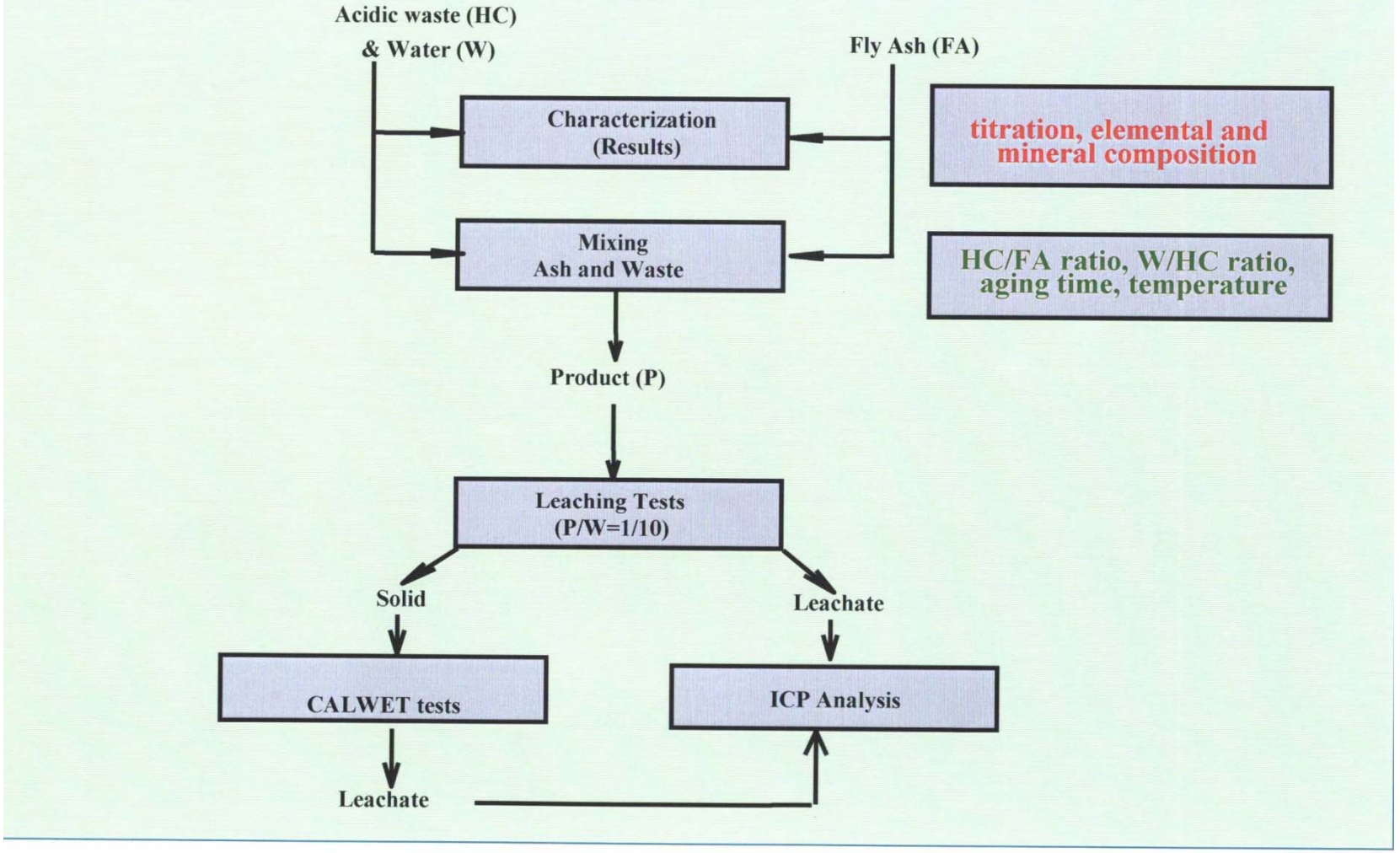
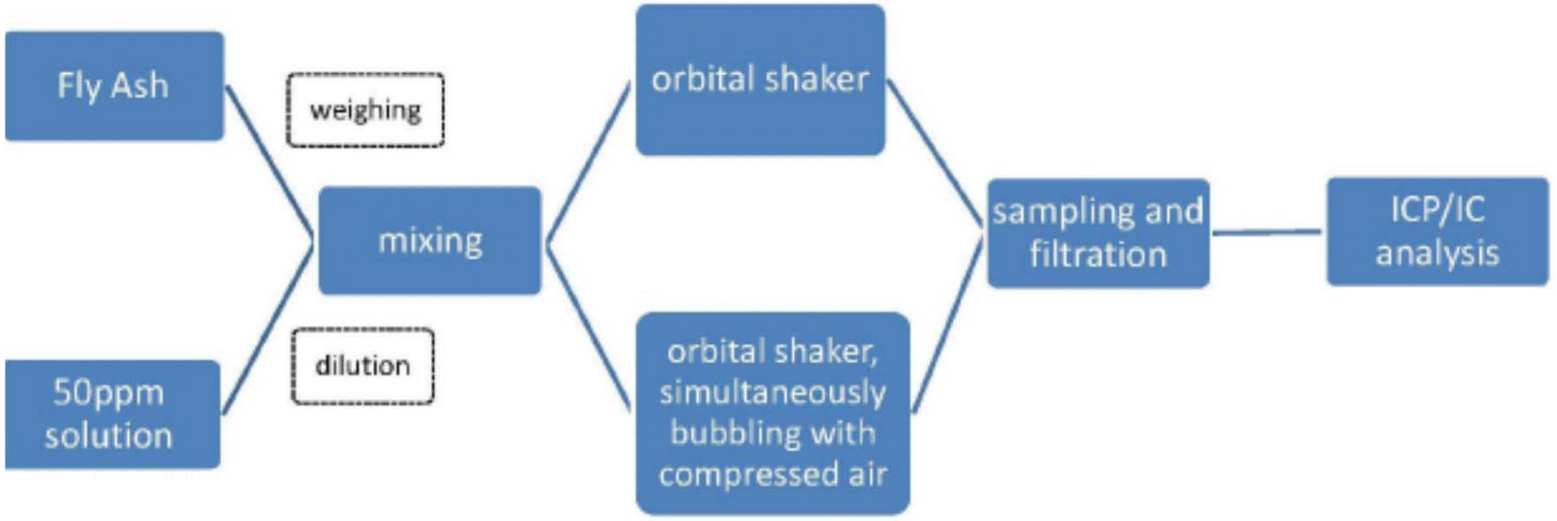
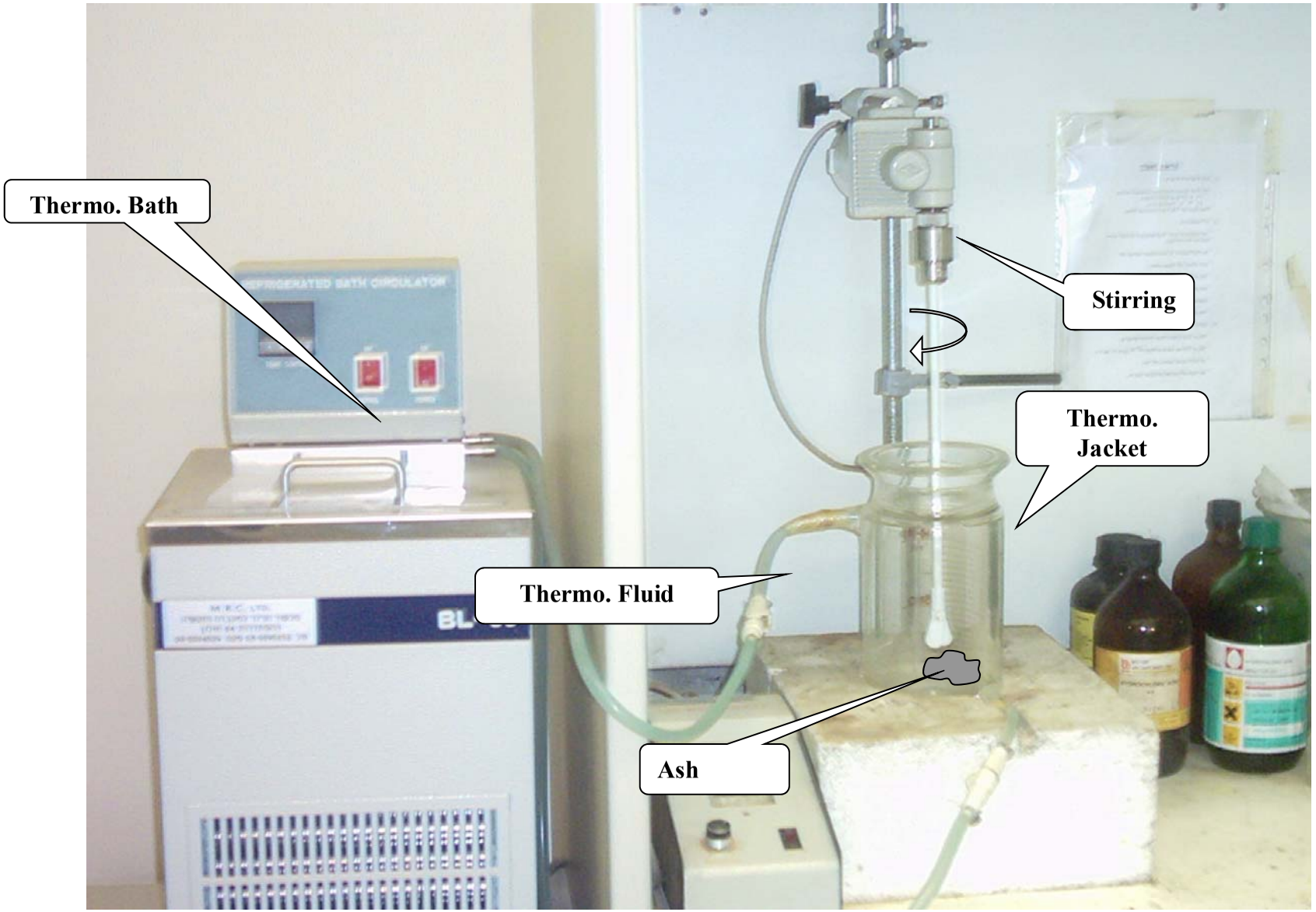
General methodology used in the study



Experimental Setup for Wastes Fixation




Thermo. Bath
Stirring
Thermo. Jacket
Thermo. Fluid
Ash

Phosphate Waste – Scrubbing Process

- Duration 20 minutes
- No Water Addition
- Solid Product

<u>Product</u>

Grey aggregate (sand like)

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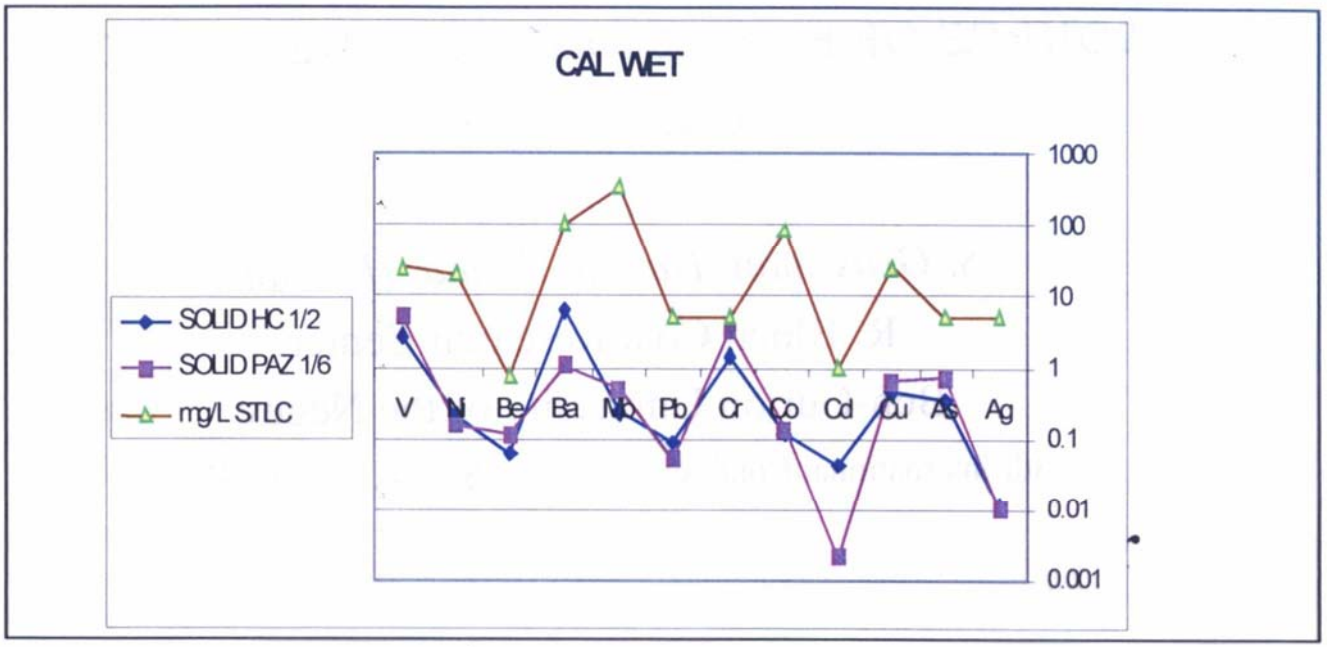
Motor Oil Sludge – Scrubbing Process

- Duration 20 minutes
- With Water Addition
- Solid Product
- Unpleasant Smell (odor fading after 3 weeks)

Product

Grey aggregate (sand like)



Aggregate Products leaching with the CALWET method

Quarry Sludge

Cutting marble stone → Sludge dust stored under water → Paste formed → Paste dried and discarded to small dry rivers

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Quarry Sludge – Scrubbing Process

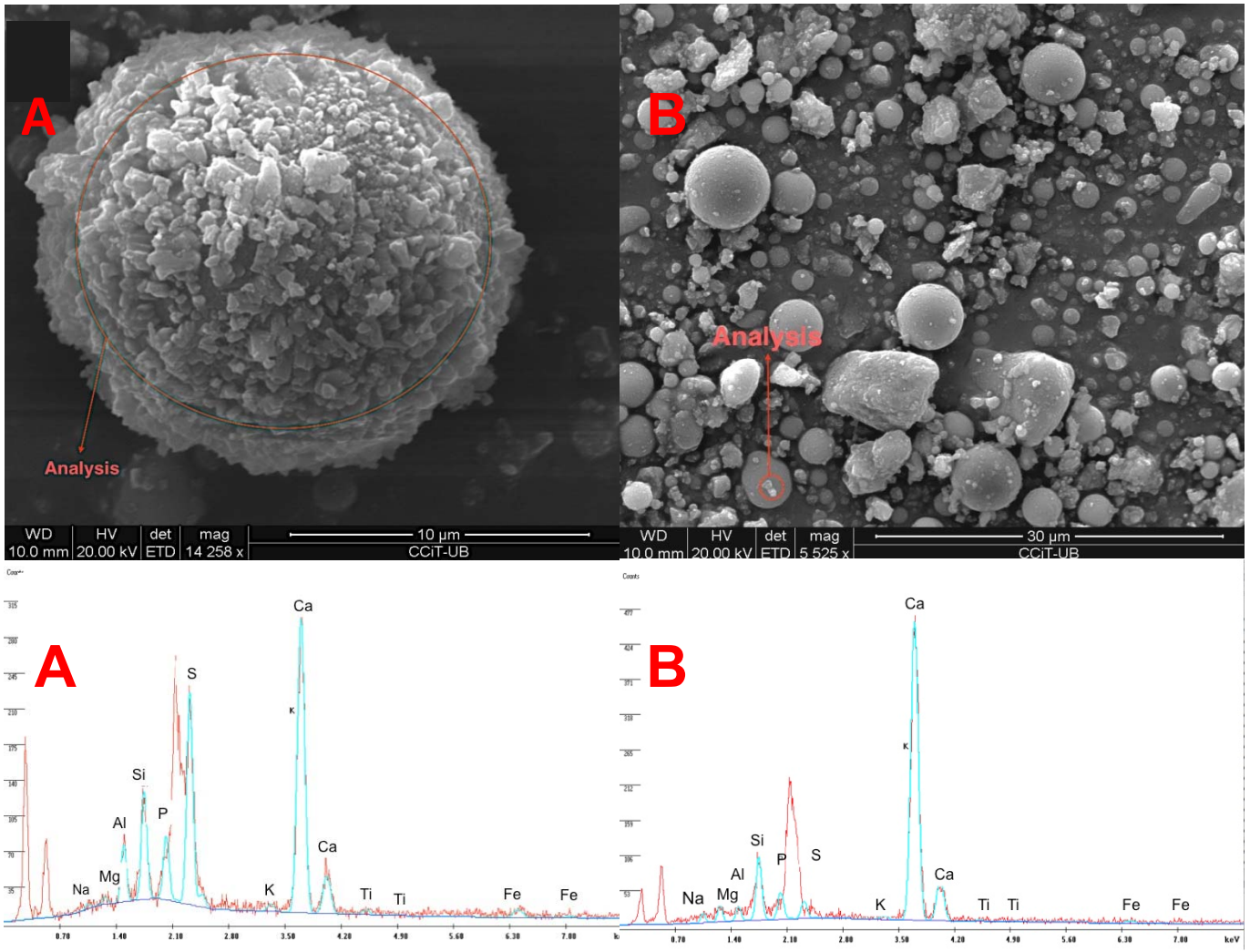
- Duration 20 minutes
- With Water Addition
- Solid Product

<u>Product</u>

Grey aggregate (sand like)

Non Hazardous Material (European Directive EN14257)

SEM and EDAX of aggregate products – (A) –with SA fly ash (B) –with CO fly ash



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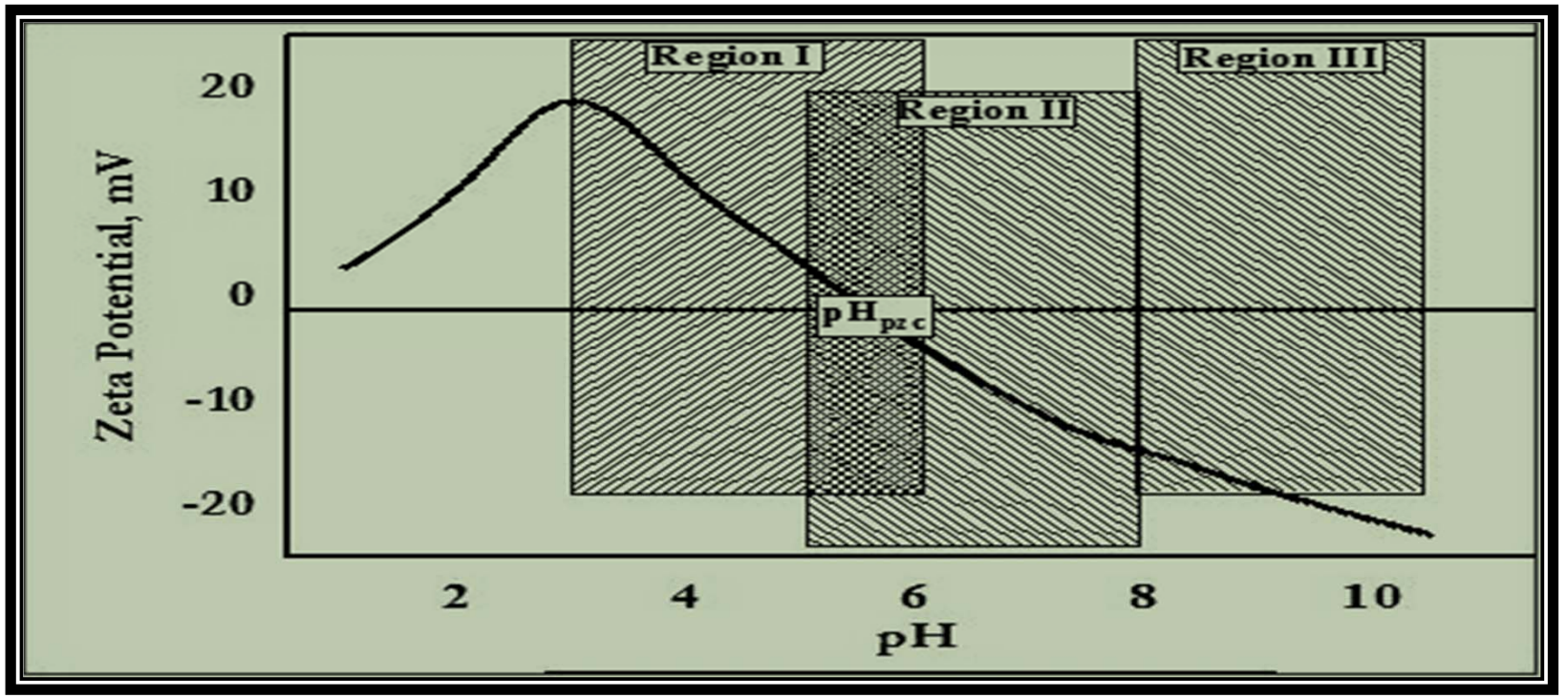
Fixation Mechanisms

- **Ion Exchange Action**
- **Chemical Bonding**
- **Electrostatic Interaction of Solids**

Metal ions interactions



- Region I: $M_aOH^0 + M_b^{2+} \rightarrow M_aOM_b^+ + H+$
- Region II: $M_aO^- + M_b^{2+}(M_bOH^+) \rightarrow M_aO^-—M_b^{2+}(M_aO^-— M_aO^-— M_bOH^+)$
- Region III: $M_b^{2+} + 2H_2O \rightarrow M_b(OH)_2 + 2H^+$

Cation exchange

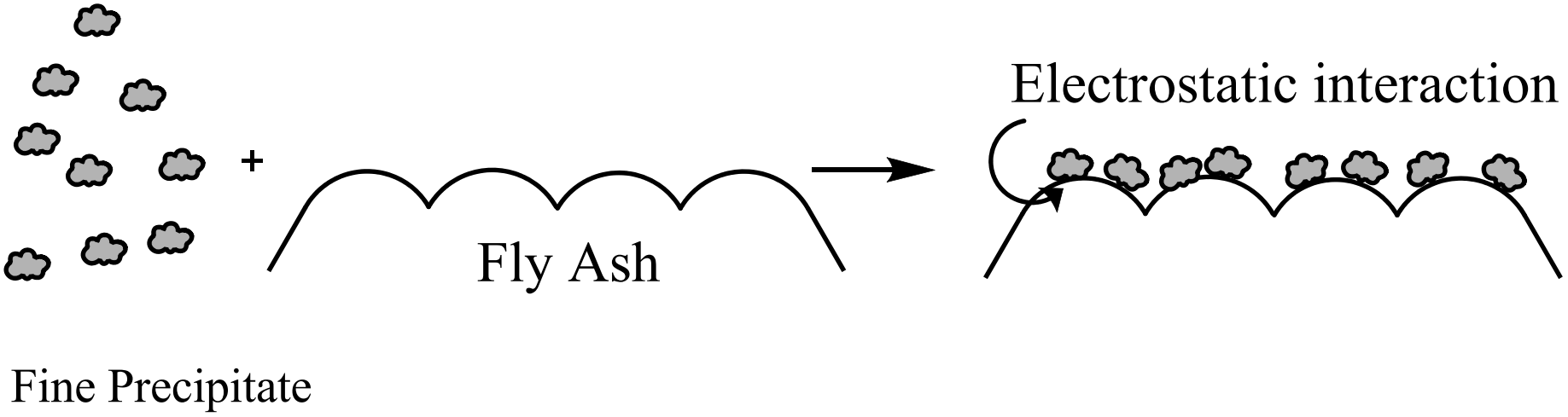
- The fly ash contains anionic groups (X^-) at the surface:

ion pairs

Ion exchange action

Precipitate interaction

- Electrostatic interaction of the precipitate with the FA surface



Coordination bonding

- The fly ash acts as ligand donor, forming complexes with the metal:
  - Mainly oxygen ions

coordination sites

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Question

Can the Scrubbed Waste be utilized as a Potential Substitute to Sand/Aggregates in Concrete?

Possible Poblems:

(i) Environmental – Leaching of Toxic Constituents

(ii) Civil Engineering – Mechanical Strength

EN 12457-2 leaching method

	Decision 2003/33/EC		
mg/kg	Inert	Non hazardous	Hazardous
SO_4	1000	20000	50000
Cr	0.5	10	70
Ni	0.4	10	40
Zn	4	50	200
As	0.5	2	25
Se	0.1	0.5	7
Mo	0.3	10	30
Cd	0.04	1	5
Sb	0.02	0.7	5
Ba	20	100	300
Pb	0.5	10	50

Scrubbed Waste Product from Motor Oil Regeneration

Scrubbed Waste Utilization

Monolits prepared from Sludge

Scrubbed Products (used as Sand Substitute, 0-20%)

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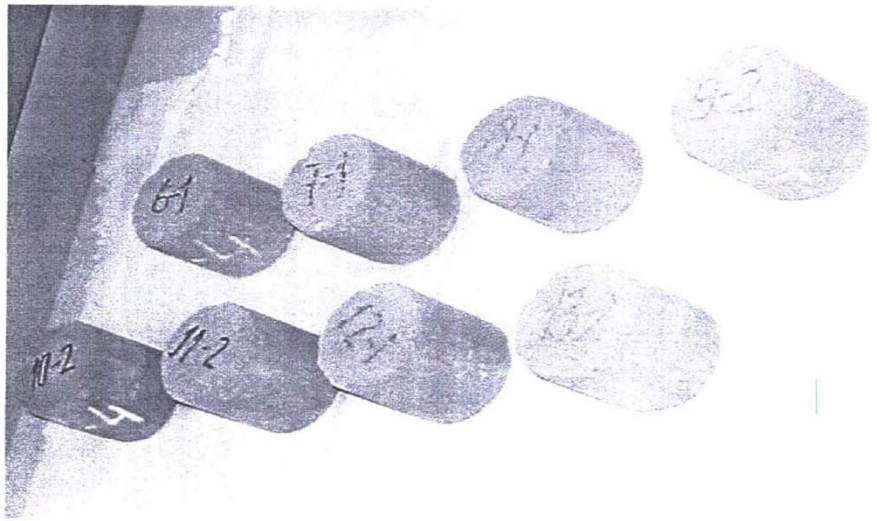
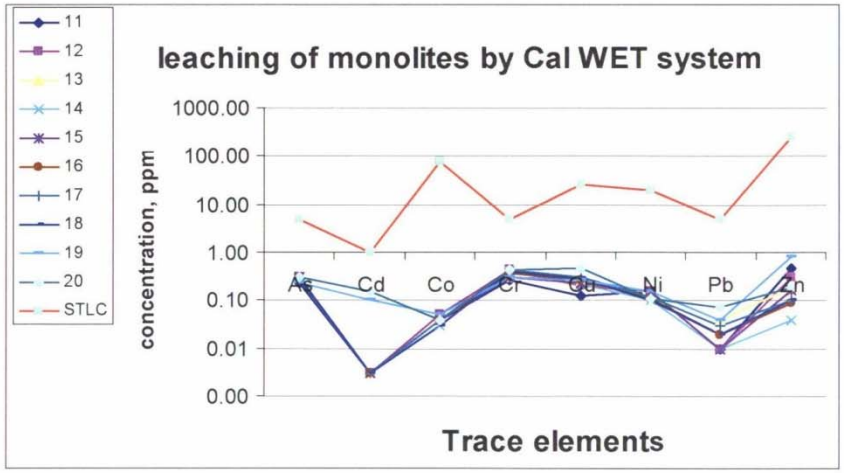
monoliths





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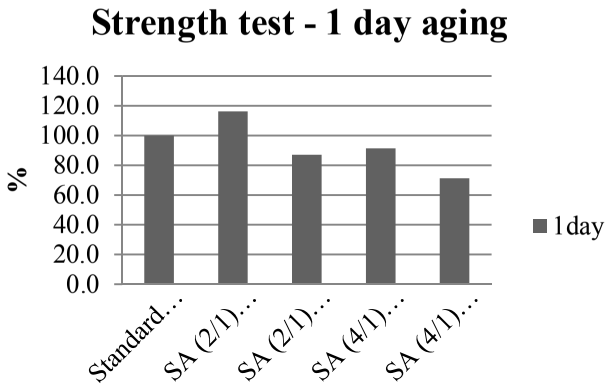
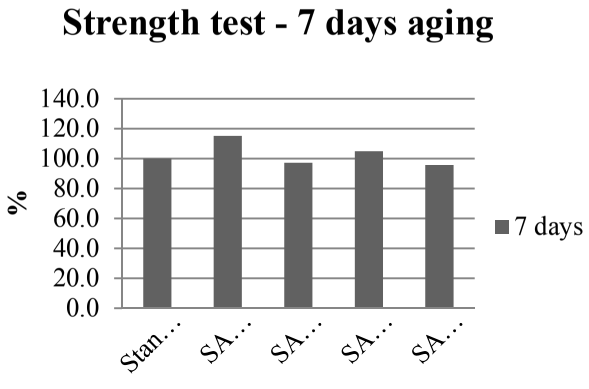
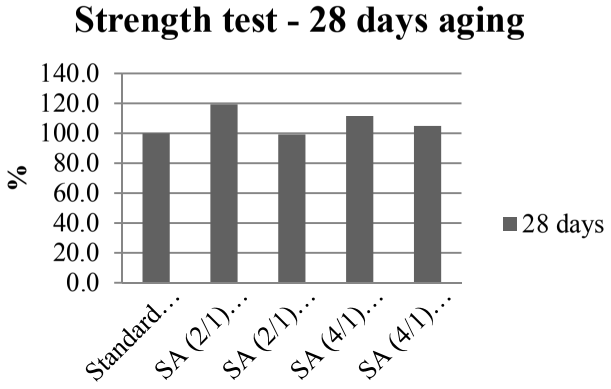
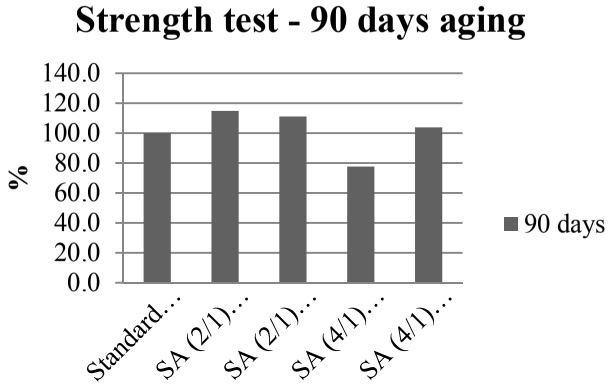
Sample	% subst in sand	Strength kg/cm^2
Ash only	0	72
Ash only	5	80
Ash only	10	98
Ash only	15	110
1:6 Sl:FA	5	52
1:6 Sl:FA	10	36
1:6 Sl:FA	15	10
1:6 Sl:FA	20	4
1:8 Sl:FA	5	66
1:8 Sl:FA	10	33
1:8 Sl:FA	15	22
1:8 Sl:FA	20	16

Scrubbed Waste Product - Phosphate Industry



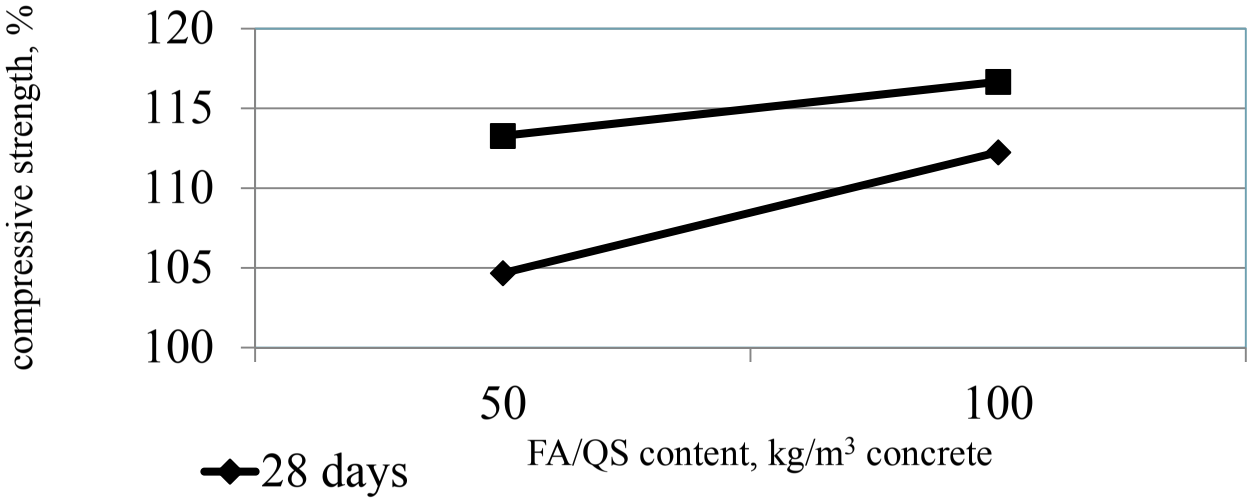






Non Hazardous Material (European Directive EN14257) •

Scrubbed Waste Product – Quarry Sludge



Non Hazardous Material (European Directive EN14257)

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Can the Fly Ash utilized as a Potential Fixation Reagent to Low Level Radioactive Waste?

Major Radioactive Wastes in Israel and Simulants Used

- ^{90}Sr

  $t_{1/2}$= 28.9 y (β^- emitter 0.546MeV) → ^{91}Y

  ^{88}Sr

- ^{137}Cs

  $t_{1/2}$= 30.17 y (β^- emitter 0.19MeV) → ^{137m}Ba→2.6m (γ emitter 0.60MeV) ^{137}Ba

  ^{133}Cs

- Actinides (^{239}Pu, ^{235}U)

  Ce (as $Ce^{3+/4+}$ salts)

Scrubbing of Actinides ($Ce^{3/4+}$)

- **20 gr SA + 400ml $Ce^{3/4+}$, 5-24hrs shaking**

$[Ce^{3/4+}]_0$=1-20 ppm → $[Ce^{3/4+}]_f$= < 0.05 ppm

$[Ce^{3/4+}]_0$=10-20 ppm (+0.1M HCl) → $[Ce^{3/4+}]_f$= 0.15 ppm

$[Ce^{3/4+}]_0$=20 ppm (+1M HCl) → $[Ce^{3/4+}]_f$= 20 ppm

Mexhanism: Precipitation + Precipitate Fixation

Conclusion: Excellent scrubbing

Scrubbing of ^{90}Sr

- **20 gr SA + 400ml Sr^{2+}, 5-24hrs shaking**

$[Sr^{2+}]_0$=1-20 ppm → $[Sr^{2+}]_f$= 3-25 ppm

Conclusion: No Scrubbing

- **Possible Solution: Precipitation as $SrCO_3$ and fixation of the precipitate**

Strontium Fixation

Scrubbing of ^{90}Sr

- **20 gr SA + 400ml Sr^{2+}, 5 hrs shaking + air bubbling + 0.5 gr Na_2CO_3 addition**

$[Sr^{2+}]_0$=2-20 ppm → $[Sr^{2+}]_f$= 0.08-0.12 ppm

Mechanism: Precipitation + Precipitate Fixation

Conclusion: Excellent Scrubbing

Scrubbing of ^{137}Cs

- **20 gr SA or CO + 400ml Cs^+, 5-30hrs shaking**

$[Cs^+]_0$=4-20 ppm → $[Cs^+]_f$= 2.5-15 ppm

Mechanism: Cation Exchange Ineraction

$$XO_y^{n-} + Cs^+ \Leftrightarrow \{XO_y^{n-}, Cs^+]\ \}$$
$$XO_y^{n-} + M^{n+} \Leftrightarrow \{XO_y^{n-}, M^{n+}\ \}$$

Conclusion: Good Scrubbing

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Efficiency as Potential Scrubber to Low Radioactive Wastes

- **Excellent for Actinides**
- **Poor for Sr^{2+}**
- **Excellent for $SrCO_3$ precipitate**
- **Good for Cs^{+}**

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Conclusions

(i) **Class F fly ash can be used as an excellent scrubber and fixation reagent for acidic wastes, trace elements and fine precipitates (fine particles)**

(ii) **The scrubbed product is a good aggregate and is environmentally green (leaching properties) and can be used as a partial replacement in the concrete or brick industry**

(iii) **It's economic value as a chemical reagent is much higher compared to it's value in the construction industry**

(iv) It is a potential good scrubber to Low Level Radioactive wastes

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