

Bituminous Coal Fly ash as a Potential Scrubber Reagent for Low Activity Radioactive Wastes

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Abstract

The most abundant fossil fuel for power generation in Israel is bituminous coal (more than 50% of the electrical power in 2011). The main waste produced during the combustion is fly ash (~10% residues). The fly ashes produced in Israel are Class F, thus when exposed to water a highly basic solution results (pH > 10.5), which is the result of the very low sulfur and phosphorus content in the bituminous coals used. Fly ashes are used commercially worldwide mainly as aggregates or as partial cement substitutes in the construction industry. The fact that the Israeli fly ash is highly basic may indicate its feasibility as a chemical scrubber for acidic wastes, which can be used as an efficient scrubber and a fixation reagent for these wastes. Furthermore it has been proved, that trace elements are trapped at the surface of the fly ash particle and also that the scrubbed waste product can serve as a partial substitute to sand and cement for concrete production. Bricks produced using the aggregate as a partial sand substitute, have proved to be strong enough according to the concrete standards and the fixation of the trace element in the concrete was excellent (checked via the improved TCLP1311, the European Directive EN12457-2 and the CAL WET methods). Subsequently, fly ash might be a potential efficient fixation reagent for radionuclides.

The feasibility of the fly ash as a potential fixation reagent for radionuclides has been studied via simulation experiments in aqueous solutions containing cesium ions, Cs⁺, divalent strontium, Sr²⁺ and Ce^{3/4+} as simulation reagents to the radionuclides (e.g Cs¹³⁷, Sr⁹⁰, and actinides). The fixation mechanisms are discussed in detail.

Keywords: fly ash, radioactive wastes, trace elements, cesium, strontium, cerium

Introduction

Israel's electricity is produced mainly by 4 coal fired power stations (>61% in 2010¹). The utilities burn about 13Mtons of bituminous coal per year. This amount of bituminous coal, produces ~1.3Mtons of coal fly ash annually. The major countries which Israel imports their coals from are South Africa, Columbia, Australia, Indonesia and Russia² and it contains ~10% of inorganic mineral materials.

The particle size distribution of coal fly ash is 3-250 μm . Fly ash particles contain different types of spheres such as cenospheres (image 1A) and plerospheres (image 1B) which are "glassy bubbles" that consist mainly of aluminum and silicon oxides. The cenospheres contain also carbon dioxide and/or nitrogen which give the ash its light weight properties. The plerospheres have similar composition as the cenospheres, but it contains other particles inside filling it. For a non-porous material the fly ash has relatively large surface area (0.97-1.2 m^2/gr) which makes it a possible potential fixation reagent.

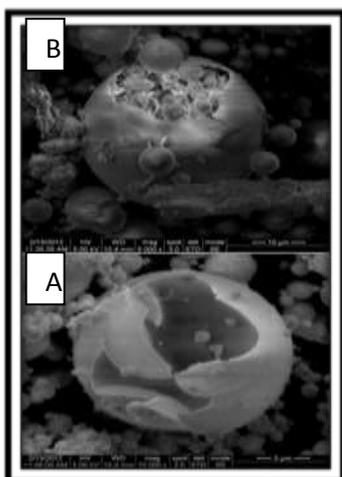
Israel has strict environmental regulations, thus the coals imported to Israel contain low content of sulfur and phosphorus. Therefore, the fly ash produced has a highly basic reaction when exposed to water ($\text{pH} > 10.5$), because of high lime (CaO) content and is defined as Class F. Due to the fact the fly ash has a high base content it is possible to use the fly ash as a chemical scrubber for acidic wastes.

The chemical composition of the South African and Columbian fly ash (SAFA, COFA) used in this study is given in Table 1.

Table 1: The Major components and Minor elements in the SAFA and COFA of the South African and Columbian fly ashes

COFA*	SAFA*	Component % weight	Element ppm	COFA**	SAFA**
54.4	40.9	SiO ₂	Ag	9.5	13.6
20.8	31.4	Al ₂ O ₃	As	<10	< 10
1.05	1.75	TiO ₂	Ba	1,150	2,350
6.18	3.05	Fe ₂ O ₃	Be	5.07	9.43
4.65	8.35	CaO	Cd	2	< 2
2.05	2.45	MgO	Co	27	40
0.12	0.05	K ₂ O	Cr	133	150
0.05	0.02	Na ₂ O	Cu	60	77
0.75	1.95	P ₂ O ₅	Mn	375	360
0.13	0.35	SO ₃	Ni	70	68
9-7	5-4	C			

Image 1: SEM images of the A- Cenosphere and B- Plerosphere



The fact that the fly ash has very good adsorption properties, due to the high surface area, created different modes of utilization such as: structural filling for road construction and stabilization of soil in agriculture.

Fly ash as a neutralization and fixation reagent for acidic waste

Recently it was shown that the fly ash can act as an effective neutralization and fixation reagent for dangerous acidic wastes³. Two wastes have been tested:

- 1) Acidic Organic waste of regeneration processes of used motor oil. This waste contains more than 10M of acid waste per liter. The waste also contains high concentration of heavy and toxic metals.
- 2) Acidic waste from the phosphate industry. This waste is a byproduct of phosphate rocks dissolution with acids (either HCl, or H₂SO₄).

The fixation quality of heavy metals inside the neutralized scrubbed waste was examined by the TCLP1311⁴ and the CALWET⁵ leaching methods. The scrubbed product that was formed was grey sand like aggregate.

The results showed that the concentrations of leached heavy metals were much under the drinking limit (DL), therefore proving that the trace elements were trapped very efficiently by the fly ashes.

These results indicate that the fly ash might act as a potential scrubber for low activity radioactive waste.⁶

Radioactive wastes

We had decided to study the fixation potential of the coal fly ash with three different types of radioactive wastes:

Cs¹³⁷ which is one of the nuclear fission byproducts of U²³⁵⁷ and has a half-life of 30.17 years. During the decay it emits β rays (0.19MeV) to form metastable nucleus of Barium (137m), which further decays fast (2.6 minutes) with emission of γ rays (0.60 MeV) to the stable isotope of Barium.

Sr⁹⁰ The strontium radionuclide is also one of the major nuclear fission byproducts of U²³⁵⁸. It's half-life is 28.90 years, which during this time it emits β irradiation (0.546MeV) and decays to a stable isotope of Yttrium (Y⁹⁰).

Actinides The Actinides which are the main byproducts during the fission are all radioactive. They are a derivative of the 5f shell and usually decay as an α emitter. A typical actinide is plutonium – Pu²³⁹ which is formed in nuclear plants⁷.

Simulants of the radionuclides

Working with radioactive material is very expensive, due to the high cost of protective measures needed to be taken. Thus we decided to work with simulants of the radionuclides. The simulants are: Cs¹³³ (A stable isotopes of Cesium), Sr⁸⁸ (A stable isotopes of Strontium) and Ce as a simulant to the actinide elements.

Experimental section

Materials and Equipment

All water used in the study was Treion Deionized Water Columns (UPDI) with a resistivity larger than 18MOhms/cm.

Chemicals:

The chemicals used were of analytical grade produced by Sigma/Aldrich, Riedel de Haen, B.D.H or Merck.

Fly ashes

South Africa (SAFA) and Columbian (COFA) fly ashes were supplied by the Utilities. The density of SAFA is 0.98gr/cm³ and that of COFA is 0.85gr/cm³.

Gases- Nitrogen (99.95%, dry) and air (dry) were supplied by MAXIMA Ltd.

Equipment

The following instruments were used throughout this study: pH-meter – of El-Hamma company model Cyberscan510. Calibration of this device was made by three buffer solutions : pH4; pH7; pH10. ICP-OES – Induced Chemical Plasma Atomic Emission spectroscopy – from Varian, model 710-ES for determination of the elements. Some of the cesium samples was analyzed in ICP-OES from Varian model VISTAPRO and some cesium samples were analyzed in ion chromatograph of Dionex model DX-500. Orbital Shakers from Cocono, model TS-400 for the leaching experiments and Teflon filters for PET syringe from Tamar LTD, model FP-030/0.2 μ were used for filtering of the solution from the fly ash samples. Analytical scales from Mettler, model AE100.

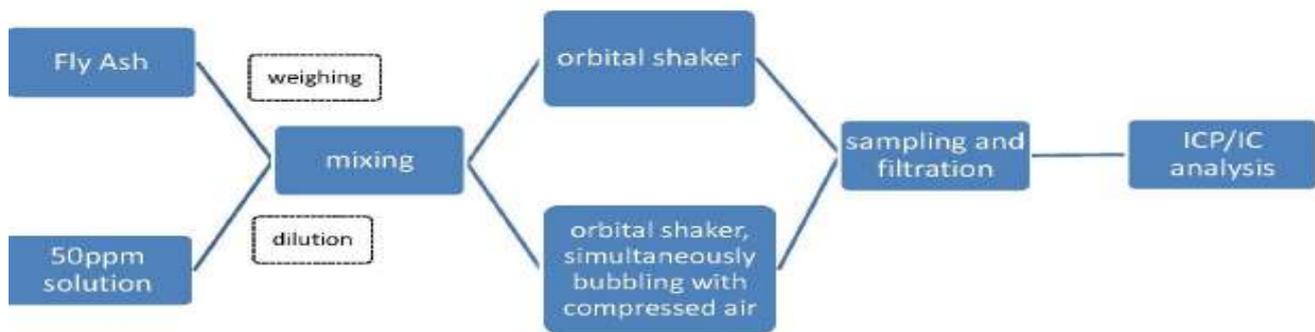
Experimental method

The experiment was carried in 6 steps (as shown in scheme 1):

- 1) Preparing a simulant solutions (Cerium, Strontium or Cesium) in a known volume.
- 2) Mixing the solution with fly ash in a PET bottle.

- 3) Mixing the mixture in the orbital shakers at 250rpm for different periods of time.
- 4) Taking a sample and filter it.
- 5) Measuring the pH and acidifying the sample to prevent precipitation.
- 6) Measuring the concentration of the simulation element studied in the ICP-OES

Scheme 1 – work method



Results and Discussion

Fixation of Ce^{3+} and Ce^{4+} with SAFA

Solutions of 20ppm of Cerium were prepared from $Ce(NO_3)_3$ or $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ salts and acidified with HCl to pH2. The mixture of the fly ash with the solution was mixed for 24 hours (Solid/Liquid ratio – 1/20, 20 gr fly ash + 400ml Cerium solution).

The mixing was carried out in 500 ml PET bottles in the orbital shaker at 250 rpm. The acidity at pH2 was necessary to prevent precipitation of Ce^{3+} or Ce^{4+} in the solution. At the end of the mixing the solution was filtered and was acidified to a pH1 with 65% HNO_3 . Finally [Ce] was measured in the ICP-AES (and is given in Tables 2, 3, and 4):

Table 2: Fixation of Ce^{3+} with SAFA in a 1:20 ratio (S/L)

Exp. number	SAFA weight (gr)	Shaking period (hr)	[Ce] ₀ ppm	[Ce] _f ppm
1	10	24	19	<0.1
2	10	24	19	<0.1
3	0	0	19	19

* [Ce]₀ concentration before mixing with fly ash, [Ce]_f concentration after mixing with fly ash

Table 3: Fixation of Ce^{4+} with SAFA in a 1:20 ratio (S/L)

Exp. number	SAFA weight (gr)	Mixing period (hr)	[Ce] ₀ ppm	[Ce] _f ppm
4	20	24	20	<0.05
5	20	96	20	<0.05
6	20	30	1 + 0.1M HCl	<0.05

* [Ce]₀ concentration before mixing with fly ash, [Ce]_f concentration after mixing with fly ash

Table 4: Fixation of Ce^{4+} with COFA in a 1:20 ratio (S/L)

Exp. Number	COFA weight (gr)	Mixing period (hr)	[Ce] ₀ ppm	[Ce] _f ppm
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7	20	24	20	16.16
8	20	48	20	<2
9	20	72	20	<0.05
10	20	96	20	<0.05

* $[Ce]_0$ concentration before mixing with fly ash, $[Ce]_f$ concentration (after shaking with fly ash) in the filtrate

From the results in Tables 3, 4, and 5 it is concluded that:

Efficient fixation of Ce^{3+} and Ce^{4+} in the fly ash is observed, the concentration of the $Ce^{3+/4+}$ was reduced from 19-20 ppm, in the mother solution to ~0.1ppm after treatment with the fly ash. Therefore, the fly ash can probably be a very effective fixation reagent for actinides (assuming Ce^{3+} and Ce^{4+} can simulate the actinides). Moreover, The fixation mechanism is probably coordination bonding as the cerium ions are soft Lewis acids.

Fixation of Cesium

Solution of 20ppm of Cesium was prepared from $CsNO_3$ Salt, mixed for different periods of time (1-24 hours) with 20 gr of fly ash (1:20 S/L ratio). The mixture was put in a 500 ml PET bottle in an orbital shaker at 250 rpm. At the end of the mixing period the samples were filtered and acidified with 65% HNO_3 to prevent precipitation. Analysis of $[Cs^+]$ was carried out in the solutions with ICP-AES (results are given in Table 5).

Table 5: Fixation of Cs with SAFA/COFA in a 1:20 ratio (S/L)

Exp. number	Fly ash Source	SAFA weight (gr)	Mixing time (hr)	$[Cs]_0$ ppm	$[Cs]_f$ ppm
11	COFA	20	24	20	14.1
12	SAFA	20	1	20	14.9
13	SAFA	20	5	20	14.4
14	SAFA	20	24	10	7.2
15	COFA	20	24	10	5.3
16	COFA	20	5	20	15.6
17	SAFA	20	24	20	14.5
18	N.A	0	0	20	20

* $[Cs]_0$ concentration before mixing with fly ash, $[Cs]_f$ concentration after mixing with fly ash

As can be clearly seen (Table 5), cesium cations (10-30% of the initial Cs^+ concentration) are adsorbed at the surface of the fly ash particles. Thus, it is concluded that there is an appreciable fixation of Cs^+ ions in the fly ash, which indicated that fly ash can act as a fixation reagent for Cesium ions. The fixation mechanism is probably that the fly ash behaves as a cation exchanger, The anionic groups on its surface are aluminates, AlO_2^- , and/or silicates, SiO_3^- .

Fixation of Strontium

Solutions of 20ppm of Strontium were prepared with $Sr(NO_3)_2$ salt. Mixture of the solution and SAFA was introduced into a 500 ml PET bottle with ratio of 1/20 (S/L). The mixture was mixed for different period of times: 5–96 hrs in an orbital shaker at 250 rpm. The results have shown that the strontium concentration is increased, which means that an appreciable leaching of strontium ions from the fly ash into the solution has occurred (due to high concentration of strontium in the fly ash ~0.5%w). Therefore, fixation is not efficient using the regular method. Due to this reason, different procedure was taken in order to trap the Strontium ions inside the fly ash. This method is to precipitate the Sr^{2+} ions as an insoluble salt (the most common is the $SrCO_3$, $K_{sp}(SrCO_3) = 5.60 \times 10^{-10} M^2$). The idea is that if successful, the precipitate will adhere to the surface of the fly ash particles.

In one set of experiments, Ex12-13, 0.5gms of Na_2CO_3 were also added to the solution and in the second set Ex 14-15, air was bubbled through the solution in order to dissolve carbon dioxide from the air into the basic

solution as carbonate ions. After mixing was completed the fly ash was filtered from the solution and a sample from the solution was taken and acidified to pH1 with 65% HNO₃ (to prevent precipitation). Finally the concentration of the strontium was analyzed with ICP-AES (as shown in Table 6):

Table 6: fixation of Sr²⁺ with SAFA in a 1:20 ratio (S/L)

Exp. number	SAFA weight (gr)	Mixing period (hr)	[Sr] ₀ ppm	[Sr] _f ppm
Na ₂ CO ₃ addition (i)	20	5	10	0.15
Na ₂ CO ₃ addition (i)	20	5	10	0.15
Air bubbling (ii)	20	5	10	0.16
Air bubbling (ii)	20	5	10	0.12
Air bubbling (ii)	0	0	10	9.86

* [Sr]₀ concentration before mixing with fly ash, [Sr]_f concentration after mixing with fly ash

From the results (Table 6) it is concluded that: indeed is an efficient fixation of Sr as the insoluble SrCO₃ salt in the fly ash. The fixation mechanism is probably by formation of fine SrCO₃ precipitate which interacts electrostatically with the fly ash surface. Thus, the strontium ion is fixed on the fly ash surface as the SrCO₃.

Conclusions

The fixation experiments show that coal fly ash can act as a very good fixation reagent for the radionuclide simulants probably via three modes of trapping: coordinative bonding (Ce), Cation exchange mechanism (Cs), and precipitate adsorption (SrCO₃).

All of the simulants showed an effective fixation in the fly ash and much more detailed experiments have to be carried out to continue checking the effectiveness of the fixation.

Acknowledgement

We would like to thank the Israel Coal Ash Administration for funding the research and to Ariel University Center and Dr. Hanan Teller for supplying us the equipment and work space.

Also acknowledgement to the Geological Survey of Israel, Jerusalem for chemical analysis and Mrs. Michal Ejenberg for the SEM analysis.

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