Leaching Investigation of Coal Fly Ash and Dry Desulphurisation Residues by Stabilization into Ash Rock

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Coal-fired power plants are producing the major percent of the electrical energy worldwide. As a result of coal combustion, a huge amount of fly ash and slag are produced that ends in landfill disposal. Also the by-products resulted from the flue gas desulphurisation plant are produced in significant quantities that also may end in the fly ash landfill disposal. In some particular cases, the fine fly ash is used in the cement industry and the FGD by-products can be used as basic material for civil construction products. The reuse of these products depends on the coal composition and the FGD technology applied. Anyway, only a small fraction of the overall production of fly ash, slag and FGD products is currently reused, and the rest ends in landfill disposal sites. One of the environmentally friendly technologies of land filling for this materials is dense slurry that creates a homogenous mixture between the combustion products and water in controlled proportions with the aim to activate the cementing reactions of pozzolanic elements found in the fly ash and calcium based elements from FGD products. The resulted product is the "ash rock" that encapsulates and prevents the leaching of the harmful elements containing in the fly ash and FGD by-products.

Keywords: coal combustion residues, fly ash, flue gas desulphurization by-products, ash rock

Power plants that are running on fossil fuels, following a long history, remain today the main source of energy [1]. The most common fossil fuel for power plants is coal. There are different types of coal, depending on the extraction site, the chemical composition and energy content [2]. Solid residues resulted from coal combustion in coal-fired power plants (CFPPs) include mainly fly ash, bottom ash, boiler slag and flue gas desulphurization by-products [3].

The quantities and properties of ash produced in a CFPP would vary significantly from case to case and will depend mainly on the type of coal used, the source of coal, the combustion technology and operating conditions, the age of the furnace/plant, as well as the type of technology used for emission control. For example, a thermal power plant with an efficiency of ~35% and using Romanian lignite as fuel (~6-13 MJ/kg LHV and ~12-28 wt% ash content [2]) will require between ~750 and 1650 kilograms of lignite to generate 1 megawatt-hour of electricity, and the resulted amount of ash will be ~90-480 kg/MWh. For a 330 MW combustion unit, typical for Romania, the coal consumption will be about 6000-13500 t/d and the ash formed can be as high as ~700-3800 t/d, of which up to 20% (in dry-bottom units [3]), will be removed as bottom ash from the base of the furnace and the remainder as fly ash from the flue gas using, for example, electrostatic precipitators [2,3].

Ash from coal combustion will consist mainly of silica (SiO_2), alumina (Al_2O_3), iron (Fe_2O_3) and calcium oxide (CaO) [2]. It will also contain trace amounts of toxic metals, such as arsenic (As), barium (Ba), beryllium (Be), boron (B), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), selenium (Se), strontium (Sr), thallium (Tl), vanadium (V) and other trace elements [2]. In addition, dioxins and polycyclic aromatic hydrocarbons (PAHs) can also be found in coal fly ash [3].

CFPPs do also produce large quantities of flue gas desulphurization by-product as result of the removal of sulphur dioxide (SO_2) from flue gas using lime-/limestone-based wet/dry FGD systems [3]. Currently, wet scrubbing is the most widely used FGD process for controlling SO_2 emissions [3]. However, recent years have shown an increased interest in the development of dry FGD systems [4], which may achieve high SO_2 removal efficiencies in plants burning low/high sulphur coals and, thus, approaching the efficiency performance of wet systems.

Composition and properties of FGD by-products are often site-specific characteristics [4]. The major sulfur-containing components of FGD by-products are calcium sulphite ($CaSO_3$) and calcium sulphate ($CaSO_4$) [3].

Emissions from CFPPs have a significant impact on all aspects of life, ranging from individual health to global climate issues. The landfill disposal of coal ash constitutes a potential threat to the environment through the leaching phenomenon and dust air pollution [5].

Regarding the environmental issues caused by land filling of huge amounts of solid residues from coal combustion, a dense slurry technology (DST) was developed. DST presumes to create a homogenous mixture between the solid residues and water in a controlled environment with the aim to activate the cementing reactions of the elements containing in the coal ash. The final product of the process is the "ash rock" that encapsulates and prevents the leaching of the harmful elements from coal combustion solid residues [6].

This research investigates the immobilization/stabilization of the harmful elements into the ash rock matrix, by using the DST technology.

Experimental part

Materials and instrumentation

For this study, fly ash samples and dry FGD by-products were supplied by the CFPP CET Sud Timisoara (Romania).

There were used fine fly ash from the electrostatic precipitator and desulphurization by-products from residue silo of the flue gas treatment unit. The CFPP is burning a low calorific brown coal extracted from Romanian coal mine sites.

The coal fly ash rock was created in a laboratory hydraulic mixer specially designed for dense slurry studying purposes. The hydraulic mixer consists of a mixing tank and a recirculation pump. The aim of

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Table 1
FLY ASH POLLUTANT COMPOUNDS

Element	Concentration (mg/kg)
As	45
Ba	378
Cd	3
Cr tot.	220
Cu	141
Hg	2
Mo	12
Ni	166
Pb	31
Sb	6
Se	6
Zn	171

Table 2
FLY ASH OXIDE COMPOSITION

Element	Concentration (wt%)
Carbon	3.90
Na_2SO_4	0.40
K_2SO_4	1.56
$CaSO_4$	2.45
CaO	8.17
MgO	1.75
Fe_2O_3	7.22
TiO_2	0.29
Al_2O_3	15.41
SiO_2	58.77
Others	0.08
$SiO_2+Al_2O_3+Fe_2O_3$	**81.4**

Table 3
FGD BY-PRODUCT COMPOSITION

Element	Concentration (wt%)
$CaCl_2$	0.06
$CaSO_3$	29.86
$CaSO_4$	32.62
$CaCO_3$	14.40
$Ca(OH)_2$ active	10.70
$Ca(OH)_2$ inactive	19.50
$Mg(OH)_2$	0.22
Al_2O_3	0.07
SiO_2	0.40

hydraulic mixer is to activate the cementing reactions of the pozzolanic elements containing in the ash as a result of intense mixing process. The mixing process develops in two phases, the first one takes place in the mixing tank where the solid residues and water are mixed by the vortex created by pump suction, and the second one which develops in the recirculation pump, where the mineral structure of the fly ash is crushed by the centrifugal driven force inducted by the impeller of the pump due to the presence of water that activates the cementing reactions.

The molding of the dense slurry ash rock sampling was made on drain vessels specially created in order to simulate a closer behaviour of an open landfill disposal. For this reason, the first layer, on the bottom of the mold, was made of sand, and the second layer was a geotextile material.

The chemical composition of the ashes was analyzed with X-ray fluorescence equipment, used to establish, on site or in laboratory, the quality and quantity of different types of geological and biological environmental probes, in different states (solid or liquid), such as: soil, vegetation, filters, sedimentation, sewage, ore, ceramics, heavy metals from different types of probes, metal alloys, etc. The equipment measurement precision is in ppm range.

The composition of leaching solution was made with different methods for each component. As for the determination of heavy metals we used ICP-MS Aurora M90 made by BRUKER. Sulphate ions were determined by the gravimetric method using barium sulphate and the chlorine was determined with silver nitrate using potassium chromate like equivalence point indicator [6].

Results and discussions

The aim of conducted experiments is to create the landfill material as ash rock with physical and mechanical properties that promote a reduction in contaminant release from the ash rock matrix trough the leaching phenomenon. Leaching can be defined as the dissolution of a soluble constituent from a solid phase into a solvent. Leaching occurs as a consequence of the chemical reactions developing at the scale of the individual incineration solid residue particles as well as of the contaminant transport processes via the fluid moving through the solid particles.

The pollutants found in chemical composition of the investigated fly ash were analyzed by FRX method. The results are displayed in table 1.

Pozzolanic activity of the fly ash is given by the siliceous and aluminous oxides content [8-10]. By definition “a pozzolan is a siliceous or siliceous and aluminous material that it self-possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide (lime) at ordinary temperatures to form compounds having cementitious properties” [10].

The chemical composition of the fly ash used in this study is shown in table 2. As can be seen, over 80% of the fly ash consists of silica, alumina and iron oxide, which will play an important role on the solidification/cementation process. The coal fly ash also contains oxides of calcium, magnesium, potassium, sodium and titanium.

FGD by-product (lime) reacts with pozzolanic compounds and develops different types of lime bearing phase like calcium silicate, calcium aluminate, calcium aluminosilicate that are subsequently hydrated in the presence of water from different hydrates. These hydrates are responsible for development of strength in ash rock as new created compound [13].

The calcium based compounds found in the FGD by-products are displayed in table 3. As can be seen, calcium sulphite and sulphate constitute more than 60%.

Hydrating and cementing reactions

The hydration reactions of fly ash main oxide compounds are developed as follows [9]:

$$SiO_2 + 2OH^- \leftrightarrow SiO_3^{2-} + H_2O \qquad (1)$$

$$Al_2O_3 + 2OH^- \leftrightarrow 2AlO_2^- + H_2O \qquad (2)$$

$$CaO + H_2O \leftrightarrow 2Ca^+ + 2OH^- \qquad (3)$$

$$Fe_2O_3 + H_2O \leftrightarrow 2Fe^{3+} + 6OH^- \qquad (4)$$

The chemical reactions taking place in the DST are as follows [11,12]:

- heavy metal oxide hydration process and calcium hydroxide partial dissolution:

$$Me_2On + n\,H_2O \leftrightarrow 2Me\,(OH)_n\ (pp) \qquad (5)$$

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + HO^- \qquad (6)$$

- generating of hydrated calcium sulphate (gypsum), fast reactions:

$$Ca^{2+} + SO_4^{2-} + 2H_2O \leftrightarrow Ca\,SO_4\,.\,2H_2O\ (pp) \qquad (7)$$

- ash rock formation (at the beginning is a fast reaction):

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 31H_2O \leftrightarrow$$
$$3CaO\,.\,3CaSO_4\,.\,Al_2O_3\,.\,31H_2O\ (pp) \qquad (8)$$

- formation of calcium silicate hydrates (slow reaction):

$$xCa^{2+} + 2xOH^- + SiO_2 + nH_2O \leftrightarrow$$
$$Ca_x{}'''\ SiO_{(2+x)}\,.\ (n + x)\ H_2O\ (pp) \qquad (9)$$

During the cementing process new unsolved minerals compounds arise. New formed mineral crystals are gradually deposited by joining to others particles in the slurry mass, which are encompassing them. The formed ash rock matrix includes pollutants inside by the adsorption phenomenon.

The reaction between fly ash and lime can be considered mostly as interface controlled. Formation of complex phases like calcium

Table 4
BATCH LEACHING TESTS
AFTER 24 h

Tracked element mg/kg d.s.*	BATCH 1		BATCH 2		BATCH 3		BATCH 4		BATCH 5	
	L:S=10L:1kg		L:S=10L:1kg		L:S=10L:1kg		L:S=10L:1kg		L:S=10L:1kg	
	mg/kg d.s.*		mg/kg d.s.*		mg/kg d.s.*		mg/kg d.s.*		mg/kg d.s.*	
	MAV*	Exp. values	MAV*	Exp. values	MAV*	Exp. values	MAV*	Exp. values	MAV*	Exp. values
As	0.5	<0.01	0.5	<0.01	0.5	<0.01	0.5	<0.01	0.5	<0.01
Ba	20	<0.01	20	<0.01	20	<0.01	20	<0.01	20	<0.01
Cd	0.04	0.268	0.04	0.346	0.04	0.325	0.04	<0.01	0.04	0.109
Cr_{total}	0.5	0.812	0.5	0.721	0.5	<0.01	0.5	0.16	0.5	0.02
Cu	2	<0.01	2	0.118	2	<0.01	2	0.069	2	0.069
Hg	0.01	<0.001	0.01	<0.001	0.01	<0.001	0.01	<0.001	0.01	<0.001
Mo	0.5	<0.01	0.5	<0.01	0.5	<0.01	0.5	<0.01	0.5	<0.01
Ni	0.4	3.08	0.4	<0.01	0.4	<0.01	0.4	<0.01	0.4	<0.01
Pb	0.5	<0.001	0.5	<0.001	0.01	<0.001	0.5	<0.001	0.5	<0.001
Sb	0.06	<0.001	0.06	<0.001	0.06	<0.001	0.06	<0.001	0.06	<0.001
Se	0.1	<0.01	0.1	<0.01	0.1	<0.01	0.1	<0.01	0.1	<0.01
Zn	4	<0.01	4	<0.01	4	<0.01	4	<0.01	4	<0.01
Chloride	800	1686	800	294.9	800	191.6	800	221.3	800	147.4
Fluoride	10	<0.1	10	<0.1	10	<0.1	10	<0.1	10	<0.1
Sulphate	1000	5647	1000	1837	1000	325	1000	297	1000	165.9
Phenol index	1	<0.04	1	<0.04	1	<0.04	1	<0.04	1	<0.04

*M.A.V – maximum allowable value for inert residues
*d.s – dry substance

aluminosilicate, calcium iron aluminum silicate cannot be ruled out [13].

The cementing reactions developed in DST are strongly influenced by:

- the intense mixing of the solid residues with a reduce quantity of water compared with solid mass, which is dissolving the calcium (CaO) oxides. The resulted solution enables partially the surface of the ash particles. The calcium hydroxide (CaOH) presence that has been noticed to be formed and is reacting with the minerals dissolved in the slurry, and with the silicate dioxide (SiO_2) and aluminum oxide (Al_2O_3), having as a result the formation of the calcium hydrates and/or calcium aluminate, known as valuable material for the cementing process.
- The presence of reducing substances as sulphate and sulphurs enables a lower value of the pH and the massive precipitation of calcium carbonate resulting in calcium and aluminum sulphate which participate also in the cementing reaction of the dense slurry.

Leaching tests

The investigated dense slurry mixtures consist of fly ash (FA), flue gas desulphurization by-products (FGD) and water (W). There were investigated five batches with different mixing ratios, namely:

- Batch 1: 50wt% FA + 50wt%W
- Batch 2: 47.5wt% FA + 5wt%FGD + 47.5%W
- Batch 3: 45wt% FA + 10wt%FGD + 45%W
- Batch 4: 38wt% FA + 6wt%FGD + 56%W
- Batch 5: 35wt% FA + 9wt%FGD + 56%W

The mixture ratio of dense slurry (DS) used in the experiments is solids to water ratio of 1:1 by weight for batches 1, 2 and 3, and 1:1.3 for batches 4 and 5. Solids particle ratios in the mixture are 75wt% fly ash and 25wt% FGD by-products.

After molding into drainage vessels, the slurries were cured under ambient conditions for 28 days. After curing period there were prepared five samples from each batch and subjected to identical exposure and testing. The water exposure time was consecutive 1, 7, 14, 28 days with a ratio of liquid to solid (L:S) of 10:1. During this time there were observed trends of several parameters like sample integrity and the specific indicators of leaching, accomplished according to SR-EN 12457-2003, and Romanian legislation expressed by Order No 95 from 12/02/2005 [14].

Leaching results after 24 hours of water exposure are displayed in table 4. As incineration residues are produced by high-temperature processes, they are thermodynamically unstable under ambient conditions. This renders incineration residues highly reactive, especially under wet conditions. The specific environmental conditions influence and change the leaching behavior and contaminant release from resulted ash rock during final landfill disposal. The application site itself then modifies the water infiltration pattern as a result of the physical and hydrological characteristics of the ash rock. Thus, the discharge pattern also depends on the pore type, pore distribution, homogeneity, permeability and field capacity of the ash rock material as well as on the presence of preferential flow paths. The integrity of the sampled batches, during water exposure on curing period reflects ash rock behavior under moisture conditions. The integrity of curried batches is displayed in figure 1.

From figure 1 it can be observed that FGD by-product concentration plays an important role in stabilization/ solidification of the ash rock. Therefore, with increasing the amount of FGD by-products in the mixture will lead to a more stable behavior.

Another measurement of samples stability is the amount of different species dissolved in water during leaching test. Figure 2 illustrates the

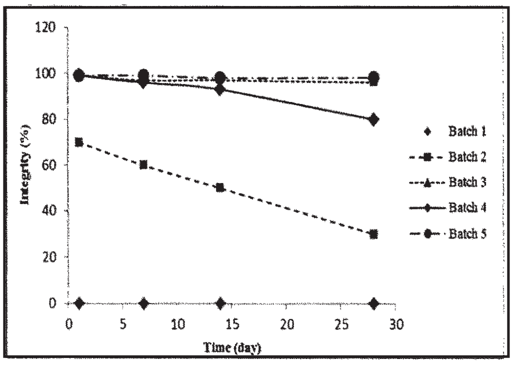

Fig. 1 Integrity of curried batches on water exposure

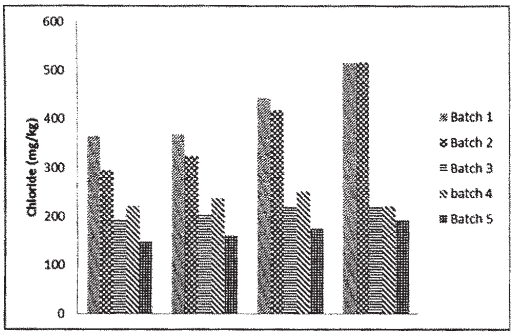

Fig. 2 Chloride concentrations during leaching tests

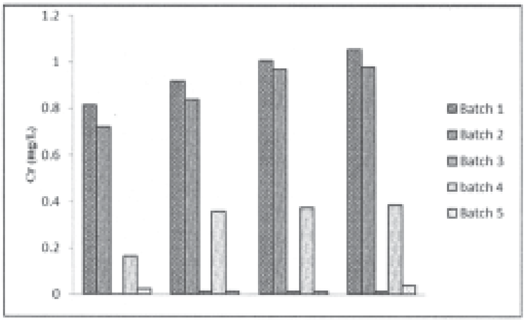

Fig. 3 Chrome concentrations in leaching solutions

evolution of chloride concentration during the tests after 1, 7, 14 and 28 days for cured samples at a L:S ratio of 10:1.

It can be observed that the stability of batches 3, 4 and 5 is better than that of batches 1 and 2. The concentration values measured within these tests were below MAV for inert waste materials.

Similarly, the concentration of heavy metals leaching solutions trends to decrease comparative with FA initial leaching (batch 1) solution as it results from figure 3.

Figure 3 shows evolutions of the chrome content in leaching solutions. Like in figure 2, batches 3, 4 and 5 were more stable comparative with batches 1 and 2. However, the results from batch 4 showed significantly higher content of chrome in the leaching solution than in batches 3 and 5. This can be attributed to lower fraction of the FGD product. It is worth noting that the concentration of chrome during the tests was below the maximum allowable value using the slurry mixtures from batches 3, 4 and 5.

The experiments also revealed no presence of nickel in leaching solutions.

Figure 4 shows the concentration of sulphate ion during the tests. As can be seen, the concentration of sulphate ion leached in solution increases for all cases. Nevertheless, the use of slurries with higher FGD product content will result in lower concentrations of sulphate ions.

Conclusions

The conducted experiments presented in this paper work are focused on the stabilization/solidification of the pollutant contained in the coal fly ash and FGD by-products into matrix of the ash rock created through dense slurry technology.

From experimental results it can be concluded that calcium based compounds from FGD by-products are highly reactive with pozzolanic compounds of the fly ash. As the amount of FGD by-products in the mixture increases the stabilization/solidification process improves. Analyzed leachate was considered after 24 h exposure according to the standard.

The results showed an increasing stability for cases 3, 4 and 5 using a higher fraction of FGD by-products in mixtures compared with case 1 and 2 for all toxic compounds. For batch 4 all toxic compounds found in the leaching solution were below MAV after 24 h of exposure to water. For batch 3 and 5 only the cadmium concentration was above MAV.

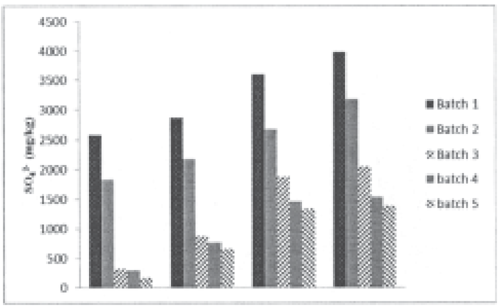

Fig. 4 Sulphate ion concentrations during leaching tests

The explanation of this pattern is the reaction inside of dense slurry and during the curing process. After these reactions a cement type of matrix is formed and the toxic compound is blocked in this matrix. These chemical reactions are responsible for decreasing trends of ion concentrations in the leaching solutions of cases 3-5.

Mixing FA with FGD through dense slurry technology minimizes the leachate flowing through disposal filling material and so the contamination of the pollutant substances on the environment. This method permits the inclusion of FA in non-hazardous materials class. The optimum composition of dense slurry is the composition of batch 4 and 5. These batches had best stability and minimum of leaching concentration of heavy metals and other toxic compounds.

Acknowledgement: The study is part of a Ph.D. program conducted by the first author at the Politehnica University Timisoara, being partially supported by the strategic grant POSDRU/159/1.5/S/137070 (2014) of the Ministry of National Education, Romania, co-financed by the European Social Fund – Investing in People, within the Sectorial Operational Programme Human Resources Development 2007-2013.

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Manuscript received: 13.05.2015