

Coal Fly Ash Activated by Waste Sodium Aluminate Solutions as an Immobilizer for Hazardous Waste

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ABSTRACT

Alkali activated coal fly ash, also known as geopolymer, is a potential low cost and low CO₂ emitting binder to replace cement in several applications. The normally used activator (NaOH, KOH and Na- or K-silicate solutions) accounts for the major raw material cost and most of the related CO₂ emission. An alternative activator was found in the aluminum anodizing process, which produces etching waste solutions containing 15-45 g/L free NaOH and 60-120 g/L Al. Thus, geopolymers were made from coal fly ash, blast furnace slag, etching waste solution and extra KOH to control alkalinity. Results show that geopolymers with a compressive strength in the range of 40 to 80 MPa can be obtained, somewhat lower than the 60-100 MPa achieved using a potassium silicate activator. This is still acceptable for an all-residue product. An additional advantage was the improved workability and extended setting time for the aluminate activator compared to the K-silicate activator. The black color of the etching solution did not have marked effects on the appearance of the product. Further research is focused on introducing hazardous waste into the mixture with the aim of immobilizing toxic components. Encouraging results have been obtained for the immobilization of lead from a slag generated by car battery recycling processes. In conclusion, there is a triple win situation, by solving the Al etching waste problem, utilizing residues from coal combustion and producing a building material with minimum CO₂ emission.

INTRODUCTION

Coal fly ash has proven to be an ideal precursor for the production of geopolymer cements. Activated in alkaline solution, compressive strengths of over 100 MPa are obtained.¹⁻⁴ In most studies Na and K silicates and NaOH / KOH are used to activate fly ash or fly ash / blast furnace slag mixtures. The activator accounts for most of the production cost of this geopolymer, so it will be a major benefit if it could be replaced by a residue solution with comparable properties.

Phair and van Deventer⁵ proposed sodium aluminate activation of fly ash to form geopolymeric binders, but this route did not get much attention until now. In the mentioned study it was demonstrated that aluminate activated geopolymers in certain cases were mechanically similar or even superior to silicate activated geopolymers. It was found that the extent of 6-coordinated aluminum in solution increases with aluminum concentration as well as with the OH/Al ratio of the solution. However, KOH promotes 4-coordinated aluminum to a far greater extent than NaOH. In the silicate chemistry of Davidovits⁶ there is only room for 4-coordinated aluminum, although it has clearly been reported that 6-coordinate aluminum does occur in geopolymer matrices.^{7,8} Thus, 4-coordinated aluminum will be more readily accepted into the silicate chemistry, which may explain the superior strength of KOH activated geopolymers over NaOH activated geopolymers. For the same reason, the addition of KOH to the sodium aluminate solutions was suggested for the present study.

A possible source of aluminate residue solutions can be found in the aluminum anodizing industry. Aluminum is anodized in a sequence of alkaline and acid baths to protect it from corrosion and give it aesthetic value. The anodizing industry is facing serious sustainability problems because of loss of primary materials, such as aluminum, sodium hydroxide and sulfuric acid and their emissions to the environment. In the etching bath the concentration of free NaOH is maintained at 55-60 g/L and the aluminum concentration is kept at 120-160 g/L. To be able to work at these concentrations, 20-25 g/L of an additive (containing 30-40% poly-alcohols to complex Al and 60-70% sodium thiosulphate to precipitate base metals) is added. Very fine suspended precipitates form in the bath, which gives the liquid a blackish color. After etching the aluminum items are rinsed. Overview of the anodizing technology and related environmental problems are given by Álvarez-Ayuso.⁹ Either the etching or the rinsing baths need to be replaced when concentrations reach their maximum working levels. These spent solutions are considered an environmental problem and are disposed of with difficulty and at considerable cost. It has been shown that zeolites and dawsonite can be synthesized from these solutions, but this requires the use of primary materials.^{10,11}

Since geopolymers have already shown the ability to immobilize hazardous liquid waste,¹² the first objective of this study is to produce geopolymers from the combination of waste etching solutions and fly ash. This would at the same time produce a geopolymer at low cost and immobilization of a waste solution considered problematic.

Further, it has also been shown that solid waste can be immobilized by replacement of part of the fly ash in geopolymer mixtures (Van Jaarsveld 1997; Pereira 2009).^{8,13,14} To take advantage from this property, a contaminated slag was tested as partial replacement of fly ash in the mixture. This slag was produced in Nigeria as a waste from the recycling process of car batteries. The slag has a high Pb content as expected, but also show contamination of As, Cd, Cr, Sb, Zn and others. The slag is currently dumped without any precautionary measure and forms a major threat to the local environment. Therefore, the second objective of this study is to include and immobilize the hazardous slag in the geopolymer matrix.

MATERIALS AND METHODS

For the experiments a class F coal combustion fly ash was used that was collected from a Dutch power station burning 14% of biomass (11% wood chips and 3% palm stones) with a coal blend. To enhance the reactivity a commercial blast furnace slag was used. Samples of car battery slag were collected from 45 cm depth at an abandoned dumpsite in Nigeria and analyzed by XRF. The analyses of the fly ash, the blast furnace slag and the car battery slag used for this study are given in Table 1. A commercial potassium silicate solution containing 25.2 wt% SiO₂ (4.19 mol/kg) and 11.7 wt% K₂O (1.24 mol/kg), giving a mole ratio K₂O/SiO₂ = 0.3 was used as activator (PQ Holland). To increase the K₂O/SiO₂ ratio solid KOH was used. Two aluminum anodizing waste solutions from Alumet BV (Etten-Leur, the Netherlands) were used as alternative activators to potassium silicate. The etching bath solution contained 119 g/kg Al and 43 g/kg free NaOH. The stationary rinsing bath solution, sampled at its highest concentration a day before discharge, was analyzed at 69 g/kg Al and 17 g/kg free NaOH. Since the Al is present as sodium aluminate, the actual Na concentration is much higher than the Na from the free NaOH. The etching bath contains approximately 20-25 g/kg of additive AD-AL-24B (AD Chemicals BV). The rinsing bath will contain the same additive in diluted form. This additive was used as well in the geopolymerization experiments. Further analytical grade chemicals KOH, NaOH and NaAlO₂ were used.

Table 1: Chemical composition of the coal fly ash, the blast furnace slag and the car battery slag used for making the geopolymers.

Wt%	Fly ash TUD-1	Blast Furnace Slag	Car Battery Slag
SiO ₂	48.94	37.17	11.4
Al ₂ O ₃	27.76	11.83	2.9
TiO ₂	2.44	0.58	0.28
Fe ₂ O ₃	7.90	0.34	42.0
MnO	0.04		0.11
CaO	6.03	42.04	0.71
MgO	1.77	7.48	0.15
K ₂ O	0.84		0.22
Na ₂ O	0.58	0.24	0.85
P ₂ O ₅	1.11		0.05
SO ₃	0.40		3.92
PbO	0.010		34.4
As ₂ O ₃	0.007		0.34
BaO	0.20		0.22
Sb ₂ O ₃			1.32
SnO ₂	0.006		0.54
V ₂ O ₃	0.042		0.01
ZnO	0.015		0.21
LOI	2.39		

For the geopolymerization experiments the solids (fly ash and slag) and liquids were separately prepared by thorough mixing. Solid reagents (KOH, NaOH and NaAlO₂) were first dissolved in the liquids. Then, the liquid was poured onto the solids and thoroughly mixed. In this way geopolymers were made from a mixture in which the weight ratio ash:slag:(water+activator solution) was kept near 30:15:20. Variations were only used in order to keep the paste workable. Extra KOH was added for studying the strength effects. For the tests with car battery slag a 5% and 10% replacement of fly ash was used in the recipe. Teflon sample cylinders of 29 mm diameter were filled with the paste to a height of about 25 mm (approximately 30 g). Mixing was done in a simple kitchen mixer, and the mixture is hold thixotropic by keeping it on a shaker. Four to six moulds were filled with the same paste and cured for 28 days at room temperature, before compression tests were performed on a Zwick Z100 tensiometer, stress controlled compression instrument (crosshead SN 149992), using testXpert software.

For the evaluation of the leaching behavior the Toxicity Characteristics Leaching Procedure (TCLP), the Dutch Compliance leaching test NEN12457-4 and the Dutch tank leaching test NEN7345 were carried out.

RESULTS AND DISCUSSION

In Table 2 the different mixtures from which geopolymer samples were prepared are presented together with their 28 day strength. Experiment #1, giving 94 MPa compressive strength is comparable with what was previously obtained with K-silicate as activator and is therefore considered the base case.⁴ With increasing replacement of KOH by NaAlO₂ the water demand increased and the compressive strength decreased, as is shown in experiments #2 and #3. When all KOH and part of the K-silicate solution was replaced (experiment #4) the compressive strength increased again and less extra water was required. It was noted that when the prepared liquid phase was allowed to stay for a few minutes before mixing with the solids, the silicate and aluminate reacted to form a gel. This explains the increased water demand and the loss of strength. By excluding K-silicate (experiment #5), the water demand was again less and also the strength increased. In general, the workability of the pastes containing NaAlO₂ was not good. The pastes did not show the thixotropic behavior that was found for the base case paste.

When replacing all K-silicate solution and part of the water by the waste aluminate solutions, the pastes were much easier to handle. With the solution from the etch bath, a compressive strength of 46 MPa was achieved (experiment #7). By using the rinsing bath solution and almost no extra water, the compressive strength went even up to almost 60 MPa (experiment #8). Decreasing the amount of slag (experiment #9) and replacing KOH by NaOH (experiment #10) resulted in a decrease of strength. So far, the anodizing waste solutions were filtered to remove the suspended particles that gave the solution its black appearance. In experiment #11 the rinsing bath solution 'as received' was used. The compressive strength decreased, but there was no coloring effect on the geopolymer samples produced. Both geopolymer samples had the same tint of grey. It seems that the particle size of the suspended particles (in the order of 10

µm) and the small quantity of suspended particles (in the order of 1-2%), allows those particles to 'hide' between the ash and slag components in the geopolymer matrix.

Table 2: Mixtures used for the geopolymerization experiments and the compressive strength of the geopolymers after 28 days curing at room temperature. The amount of water in the first column is used to prepare the liquid phase, the water in the second column is added during mixing when it was experienced that the paste was too dry for proper mixing.

Exp #	Solids (g)			Liquid components (g)					Compressive Strength (MPa)
	Fly Ash	Slag	Water	K-Sil	KOH	NaAlO ₂	Etch bath solution	Rinse bath solution	
1	30	15	10	8	2				94
2	30	15	10	+11	8	1.25	1		25
3	30	15	10	+15	8	0.5	2		3
4	30	15	13	+6.25	3		4		21
5	30	15	14	+1.25			4		31
6	30	15	14	+2.5			4	0.25 ³	38
7	30	15	8.25	+1.25		2.25		9.5	46
8	30	15	1.25			2.5		17.5	59
9	35	10	1.25			2.5		17.5	43
10	30	15	1.25			2.1 ¹		17.5	49
11	30	15	1.25			2.5		17.5 ²	39
12	30	15	15.05			2.95			26

¹ NaOH; ² unfiltered solution; ³ AD-ANO-AL-24B.

In experiment #6 a small amount of the aluminum etching bath additive AD-AL-24B was added with the intention to influence workability and setting time. The paste was indeed better workable, the setting time increased from 10 minutes to about half an hour and even compressive strength increased. The poly-alcohols contained in the additive formed aluminum complexes and may thereby have retarded the reaction. However, since no influence of this additive was experienced when synthesizing zeolites from the same solutions, this seems not very likely.¹⁵ This is supported by an experiment whereby Na-gluconate was added to the paste and much less effect on working time was noted. Another possibility could be that the thiosulfates present in the additive react with readily available Ca-ions from the fly ash to form gypsum. This would avoid the formation of calcium aluminate hydrates, the hardening minerals in calcium aluminate cements. But, as Phair and van Deventer show that sodium aluminate solutions contain considerable 6-coordinate aluminum at high pH, this would rather favor the formation of calcium aluminate hydrates in which aluminum is in the 6-coordinate state.⁵ However, the presence of the thiosulfates may have promoted the formation of calcium sulfo-aluminates in which aluminum is also present in the 6-coordinate state. These phases were indeed found in sodium aluminate activated slag.⁵

Pastes that contain waste etching solutions show a better workability than pastes with potassium silicate. When excess silica is available in solution, liberation of alumina may quickly result in the formation of sialate chains to form precursors for geopolymeric

networks. The paste will become thicker and the setting point quickly reached. However, when aluminate is present instead of silica, it will take time before there is enough silica liberated from the ash to give a suitable Si/Al ratio to form geopolymeric gels. So, it will take longer for the paste to thicken and settle.

In experiment #12 ash and slag were activated by KOH alone. The lower strength shows that the aluminum anodizing waste solutions indeed do have a positive effect on strength development. The potassium silicate activated fly ash (#1, 94 MPa) is stronger than the sodium aluminate / KOH activated geopolymer (#8, 59 MPa) followed by the sodium aluminate activated fly ash (#5, 31 MPa). This is in fair agreement with literature values of 77 MPa, 51 MPa and 18 MPa respectively using analytical grade reagent activators.⁵

Tests were repeated with increasing amounts of rinse bath solution (a new batch) by using 10 M solutions of NaOH and KOH. For practical reasons this is much more convenient than using solid KOH and NaOH pellets to be dissolved in the liquid components. Results shown in Table 3 are in agreement with was concluded above, taking into account the slight differences in compositions of the pastes. It shows also that replacing half of the water already accounts for most of the strength increase compared to activation by NaOH or KOH only. The full replacement of water by the rinsing bath solution results in only a small further increase in compressive strength. The differences between NaOH based and KOH based geopolymer are not significant from those tests, neither is the influence of filtration of the rinsing bath solutions. When no NaOH nor KOH solutions are used, but instead the rinsing bath solutions as the only liquid component, that is an 'all waste geopolymer', still a remarkable 54-59 MPa compressive strength is found.

Table 3: Liquid mix components based on 30 g of fly ash and 15 g of blast furnace slag and 28 days compressive strength.

Exp #	Water	NaOH 10 M sol	KOH 10 M sol	Rinse bath solution	Compressive Strength (MPa)	
					Filtered	Unfiltered
13	17	3			17	17
14	8.5	3		8.5	64	66
15		3		17	76	71
16	17		3		13	13
17	8.5		3	8.5	63	66
18			3	17	66	67
19				20	54	58

The experiments with 0, 8.5 and 17 g of rinse bath solution (#13-14-15 and #16-17-18 in Table 3) form a series with increasing initial mobile Al content in the mixture. Although the NEN12457-4 leaching test is intended for environmental assessment, the leaching behavior of major elements provides an insight in the process of geopolymerization. Figure 1 shows the change in leaching of Si, Al, K, Na, Ca and Mg for the two rinse

solution replacement levels compared to the water based geopolymer for the NaOH based series of geopolymers (#13-14-15). Whereas the initial mobile Al content increases, the remaining free Al as leached out of the geopolymers produced, reduces considerably. At the same time the Si leaching more than doubles, indicating that with increasing amount of aluminum rinse solution Si is more and more replaced by Al in the geopolymeric chains. The accompanying charge deficiency is corrected by including more cations in the structure. The decreasing leaching of Ca, Mg and Na illustrates this. The greatest difference in leaching is made from experiment #13 to experiment #14 and this corresponds to the largest step in compressive strength increase. However, this effect may also be due to a greater amount of geopolymer matrix formed, yet to be investigated.

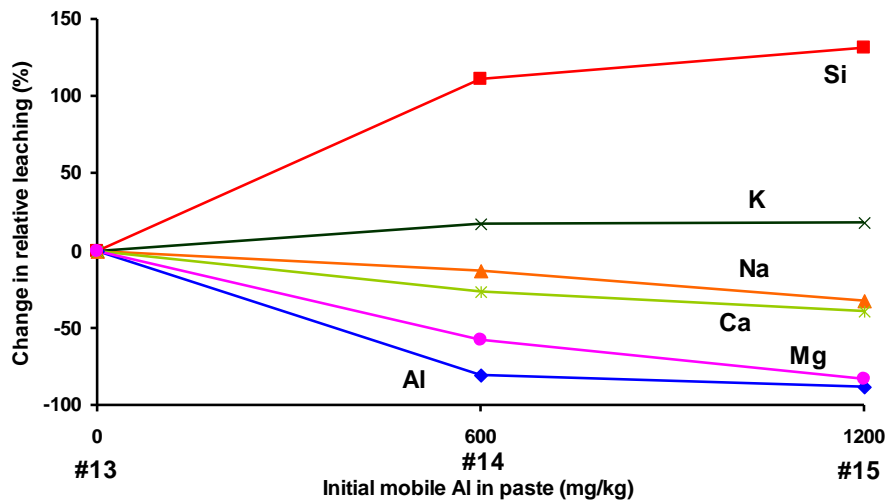


Figure 1: Changes of relative leaching (according to NEN12457-4) with increasing initial Al content in the mixture as is obtained by introducing the aluminum rinse solution. Al leaching decreases whereas Si leaching increases showing the dislodgement of Si by Al in the geopolymeric chains as more Al is initially available. The decrease in relative leaching of Ca, Mg and Na accounts for the cations required for charge balancing.

A potassium silicate based geopolymer (similar to #1) and an aluminum rinse solution NaOH based geopolymer (#15) were used as the base case for testing the effects of including the polluted car battery slag. For this purpose two new series were prepared using 0, 5% and 10% of replacement of fly ash by car battery slag. As shown in Table 4, the introduction of this amount of car battery slag had no effect on the compressive strength of the resulting geopolymer. It must be noted that the obtained strengths are somewhat higher than those found in the earlier experiments #1 and #15.

Table 4: Mix proportions for the experiments with car battery slag and 28 days compressive strength.

Exp #	Fly ash	Car Battery Slag	Blast Furnace Slag	Water	NaOH 10 M sol	K-silicate solution K ₂ O/SiO ₂ =0.8	Rinse bath solution	Compressive Strength (MPa)
20	30		15	10		10		110
21	28.5	1.5	15	10		10		113
22	27	3	15	10		10		106
23	30		15		3		17	84
24	28.5	1.5	15		3		17	85
25	27	3	15		3		17	83

Geopolymers made from fly ash and blast furnace slag and activated with waste aluminum rinse solution passed the Dutch Soil Quality Regulation emission limits and the TLCP regulatory limits for all elements.

When adding car battery slag, the NEN12457-4 leaching test on crushed geopolymer revealed that cations, including Pb, were more than 90% immobilized compared to the leaching of the unreacted starting materials. For some oxyanion forming species such as Mo and Se the immobilization was less than 50% and in some cases leaching was even higher than for the unconsolidated starting solids. However, the intention is to use the products as monoliths and therefore leaching results of the Dutch tank leaching test NEN7345 seem more relevant. It was shown that the cumulative concentrations from the eluates were all below the emission limits stated in the Dutch Soil Quality Regulation, except for Se and Sb in some samples.

All elements specified and determined are below the TCLP regulatory limits except Pb at the 10% car battery slag addition.

CONCLUSION

The present study shows that apart from the commonly used silicate solutions geopolymers can also be synthesized from aluminate solutions. By using primary sodium aluminate solutions pastes were not well workable, but by incorporating waste aluminum etching solutions from the aluminum anodizing industry workability and also strength improved. The additives used in the etching baths seem to have a positive effect on workability. Workability is even better compared to silicate activated geopolymers, which can be explained by the longer time required for reaching a certain threshold Si concentration marking the offset of hardening. The incorporation of waste aluminum etching solutions resulted in geopolymers with compressive strength in the order of 50-85 MPa.

Geopolymers form powerful waste stabilization matrices. Waste aluminum rinse solution activated geopolymers pass the applied leaching tests for all elements. Inclusion of the suspended black particles in the geopolymers did not cause a sensible change in the grey colour of the products. Expensive disposal of a major waste from the anodizing

industry is thus no longer required and the production of an 'all-waste' geopolymer will be an important contribution to the sustainability of the aluminum anodizing industry.

Even with an up to 10% replacement of fly ash by the heavily polluted car battery slag, leaching from the geopolymers produced is reduced significantly compared to the unconsolidated solids. Only with 10% replacement the Pb regulatory limits for TCLP are surpassed. Considering the tank leaching for monoliths according to NEN7345 only for some samples values for Sb and Se are found above the limits of the Dutch Soil Quality Regulation.

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