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## PERFORMANCE OF ALUSILICA AS MINERAL ADMIXTURE IN CEMENTITIOUS SYSTEMS

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### Abstract

This paper presents a preliminary study of the effect of alusilica (ALS) as a mineral admixture on the fresh properties and development of mechanical properties of cementitious systems. Cement was substituted with ALS with the ratio of 10% during grinding or blended during mixing. The produced ALS-substituted powder was studied by scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX). Flow of the fresh mortar, air content and mechanical properties of the hardening mortar were measured. The results show that the inclusion of ALS in the mortar as a mineral admixture resulted in a higher air content and lower flowability in comparison with the reference mortar. Mortar with ALS substitution, exhibited a lower compressive strength as compared to the reference mortar. This can be accounted for by the higher air content. By appropriately adjusting the flow of the fresh mortar, it is believed that ALS can be a useful cement substitution.

### 1. Introduction

Today supplementary cementitious materials, such as silica fume, fly ash and blast furnace slag are widely used in concrete. In many cases supplementary cementitious materials have an origin as problematic industrial waste products, but when these materials are properly utilized in concrete they may become very valuable through improvement of concrete properties and they may also lead to an overall reduction in CO<sub>2</sub> emissions.

Alusilica (ALS) is an industrial by-product from the production of aluminium fluoride (AlF<sub>3</sub>). ALS consists of mainly amorphous silicon dioxide, a chemical compound which is known to be useful as mineral admixture in concrete. The ALS also contains some fluorides (~5 wt%), notably in the form of aluminium fluoride, which may cause problems in cementitious systems [1]. However, this fluoride can be made chemically inert through a simple reaction with CaO. ALS can potentially be used as a mineral admixture in concrete. A preliminary

investigation took place as a BSc project in 2015 with encouraging results but also with a number of issues which needed further investigation [2].

In this paper the effect of ALS as a mineral admixture on the fresh properties and development of mechanical properties of cementitious systems is examined. A more detailed description of the investigation is given in [3].

## 2. Materials

Aalborg Portland cement clinker and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) are used. The mineral composition of the cement clinker is listed in Table 1. ALS is provided by the company Alufluor, Sweden. In the original by-product form, the ALS contains some fluoride, mainly as aluminum fluoride. To avoid free fluorides the ALS has been further processed by mixing it with CaO in hot water. This makes the fluoride precipitate as calcium fluoride ( $\text{CaF}_2$ ) which is inert in cementitious systems. The composition of raw and fluoride stabilized ALS is measured by X-ray fluorescence (XRF) and the result is shown in Table 2. The moisture content in the fluoride stabilized ALS is 4.8%. The ALS is dried to a constant mass at  $105^\circ\text{C}$  before use. CEN standard sand and demineralized water is used.

Table 1: Mineral composition of white Portland cement clinker.

Component	$\text{C}_3\text{S}$	$\text{C}_2\text{S}$	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$
Content (wt%)	77	16	5	1

Table 2: Composition of raw and fluoride stabilized ALS according to XRF.

Content (wt%)	F	Al	$\text{SiO}_2$	Ca	LOI
Raw ALS	4.9	2.1	85	-	8
Fluoride stabilized ALS	6.2	1.9	73	8.7	10.2

Mix proportions are given in Table 3. The water/binder-ratio is 0.5 and binder/sand-ratio = 1:3 for all mixes. The level of substitution was 10% ALS relative to the total binder mass. Three binders are investigated:

- 1) Reference (co-ground clinker and gypsum),
- 2) ALS-substituted, co-ground (co-ground clinker, gypsum and ALS),
- 3) ALS-substituted, blended (co-ground clinker and gypsum, subsequently blended with ALS).

Table 3: Mix proportions of mortars [g].

	Clinker (95%) + gypsum (5%)	ALS	CEN- standard Sand	Demineralized Water
Reference	450	0	1350	225
ALS-substituted	405	45	1350	225

### 3. Methods

The clinker and gypsum were initially crushed with a jaw crusher followed by disc milling (particle size < 0.5 mm) and subsequently mixed homogeneously. Further grinding was done by ball milling. For each 1 hour ball milling the Blaine specific surface by a HMK-C1 Blaine Fineness Air Permeability Apparatus and the sieve residue at the 50  $\mu\text{m}$  sieve was measured [4]. After ball milling of the reference binder for 4 hours, the specific surface area,  $S$ , was 358  $\text{m}^2/\text{kg}$ , which is in the desired range 300-400  $\text{m}^2/\text{kg}$ . Therefore, the total ball milling time, 4 hours, was used for the rest of the batches. The specific surface and 50  $\mu\text{m}$  sieve residue of the co-ground clinker and gypsum are listed in Table 4. For ALS-substituted, co-ground the same ball milling time as for reference is used since this would imply the same energy input during processing.

Table 4: The specific surface and 50  $\mu\text{m}$  sieve residue of co-ground clinker and gypsum

	Reference						co-ground ALS
Grinding batch	1	2	3	4	5	6	1
Specific surface ( $\text{m}^2/\text{kg}$ )	358	380	367	365	360	370	387
50 $\mu\text{m}$ sieve residue (%)	0.39	0.35	0.37	-	-	-	0.01

Mixing was done in a 20  $\ell$  epicyclic mixer. For ALS-substituted, blended, cement and ALS were initially dry mixed for 5 min. For the other two mixes no initial mixing of the binder was relevant. A low mixer speed ( $140 \pm 5 \text{ min}^{-1}$ ) was used during addition of the water to the binders. After 30 s of paste mixing, the sand was added during the subsequent 30 s. The mixer was switched to high speed ( $285 \pm 10 \text{ min}^{-1}$ ) and mixing was continued for another 30 s. The mixer was stopped for 90 s to remove the mortar adhering to the walls of the bowl and mixing was subsequently continued at the high speed for a further 60 s.

Immediately after mixing the flow table test was done according to ASTM C1437-15 [5]. Casting was done in standard mortar molds  $4 \times 4 \times 16 \text{ cm}^3$  and cured in a room with 95% RH, 21°C. The mortar samples were demolded 1 day after casting, and the air content of each sample was determined by weighing over and under water. Subsequently, the mortar samples were immersed in lime saturated water (19°C) until further testing [6]. The mechanical testing was in general in accordance with EN 196-1 [7]. Mechanical properties were measured at 1, 2, 3, 7, 14, 28, 56 and 112 days. Scanning electron microscopy and energy dispersive X-ray analysis (element mapping) were performed on some of the powder materials in order to examine to what extent the ALS agglomerates were broken by the co-grinding process.

### 4. Results and analysis

Table 5 lists the results of consistency of fresh mortar measured by flow table and air content of hardened mortars. Fig. 1 shows the relationship between flow value and air content by weighing of the three mortars. Clearly ALS substitution of cement leads to a lower flow percentage (defined in [5]) and a higher air content, most likely due to the stiffer mortar which more easily encapsulates air during mixing and which is less likely to release it again during casting and vibration.

Table 5: Test results for fresh and hardened mortars.

	Reference	ALS-substituted, co-ground	ALS-substituted, blended
Flow percentage (%)	124	103	61
Air content by weighing (%)	0.86	2.20	4.87
Density (g/cm <sup>3</sup> )	2.33	2.26	2.19

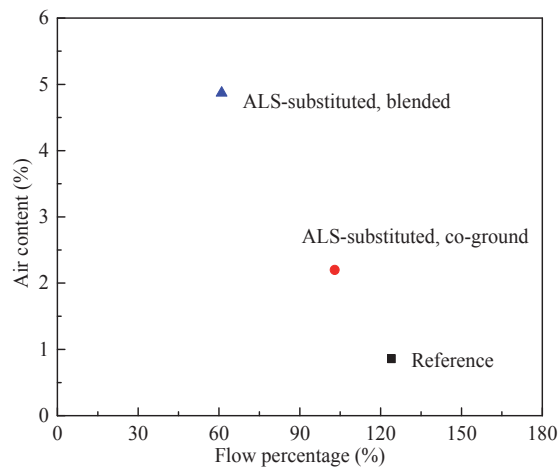


Fig. 1. Air content vs. flow percentage of fresh mortars.

The flexural strength of mortars is shown in Fig. 2. Taking into account the fluctuations on the individual measurements and the measurements as a time series, there does not seem to be a marked difference in the flexural strength between the three mixes. There may be a slight tendency towards a lower flexural strength of the mortar with ALS-substituted, blended, and perhaps a slight tendency towards a higher flexural strength of the mortar with ALS-substituted, co-ground, but the effect, if any, is minor.

The compressive strength of mortars is shown in Fig. 3. It can be seen that the samples ALS-substituted, co-ground and blended have a lower compressive strength throughout the considered time range. Compared with the reference mortar the reduction in compressive strength of samples with co-ground and blended ALS at 28 days were 11% and 15% respectively. The strength reduction for samples with ALS-substituted, co-ground is less pronounced than for samples with ALS-substituted, blended. This may have several explanations including a better dispersion of co-ground ALS and thus better reactivity of the ALS and better pore filling in between the cement particles. Also breakage of ALS agglomerates and dispersion of the particles may enable them to better act as nucleating sites and thus improve the hydration progress of the cement [8].

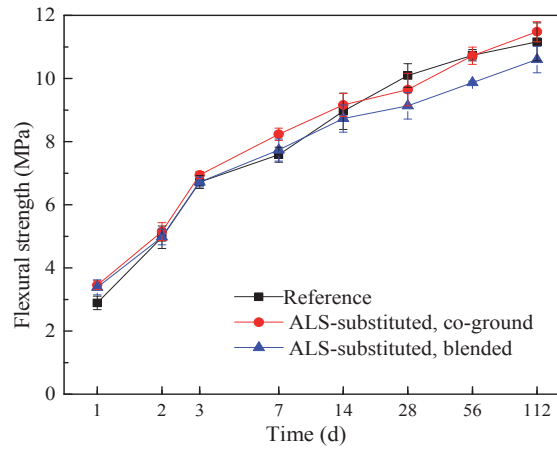


Fig. 2. Flexural strength of the three mortars.

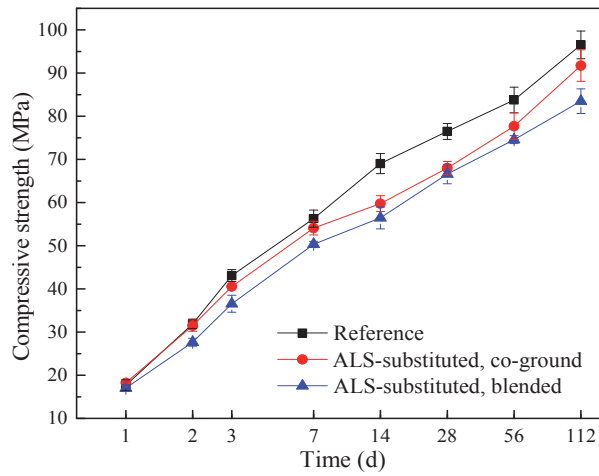


Fig. 3. The effect of ALS substitution by co-grinding and blending on the compressive strength of hardening mortars.

Another important factor concerns the observed, different air contents, which seem to be related to the differences in workability, and apparently strongly influenced by the presence and form of ALS present in the mortar. It is known that an increase in air content of 1% leads to a reduction in compressive strength by 5% [9]. Therefore, by taking the factor of air

content into consideration, the results of compressive strength can be corrected for differences in air content. Such corrected results are shown in Fig. 4. This comparison is relevant as it will be possible to correct the workability of the different mortars by means of plasticizer adjustment, and thus most likely eliminate the differences in air content. For the corrected results in Fig. 4 it is seen that the strength reduction by ALS substitution apparently can be fully accounted for by the extra air in the samples.

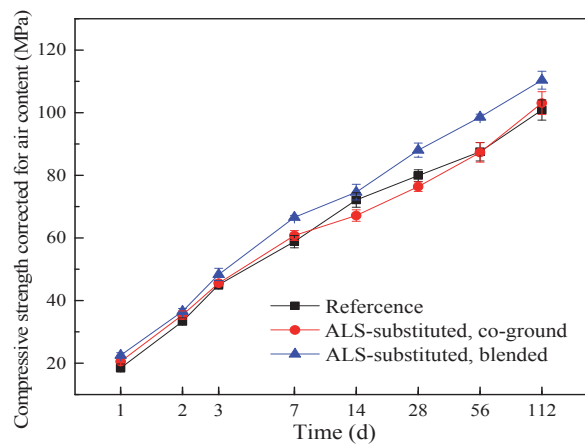


Fig. 4. The effect of ALS substitution by co-grinding and blending on the compressive strength of hardening mortars. The results are corrected for the influence for air content

SEM images were captured to investigate if the ALS agglomerates were broken by the co-grinding process, see Fig. 5 and Fig. 6. As seen from Figure 5 (top left), the ALS powder consist of agglomerates of particles mainly in the size range from a few micrometer to about 50  $\mu\text{m}$ . Relative to the ALS powder, the cement particles are slightly finer. From the EDAX maps it is possible to identify main components in the ALS co-ground system:  $\text{C}_3\text{S}$  (high Ca, some Si),  $\text{C}_2\text{S}$  (medium high Ca, some Si),  $\text{C}_3\text{A}$  (high Ca, some Al), ALS (no Ca, high Si), gypsum (high S). All ALS particles found in Fig. 6 (brightest intensity in the Si map and “no” intensity in the Ca map) are in the size range of a few micrometer. In the SEM image of ALS, Fig. 5, a multitude of particle sizes from micrometer size to about 50  $\mu\text{m}$  is found. A comparison of Fig. 5 and Fig. 6 thus clearly shows that in the ALS co-ground binder the ALS agglomerates have been broken down to particle sizes of a few micrometer. The ALS particles appear to be well dispersed in the cement system. These microscopic observations are in accordance with the measured differences regarding flowability and air contents – and further the mechanical properties – between the co-ground and blended ALS-substituted mortars.

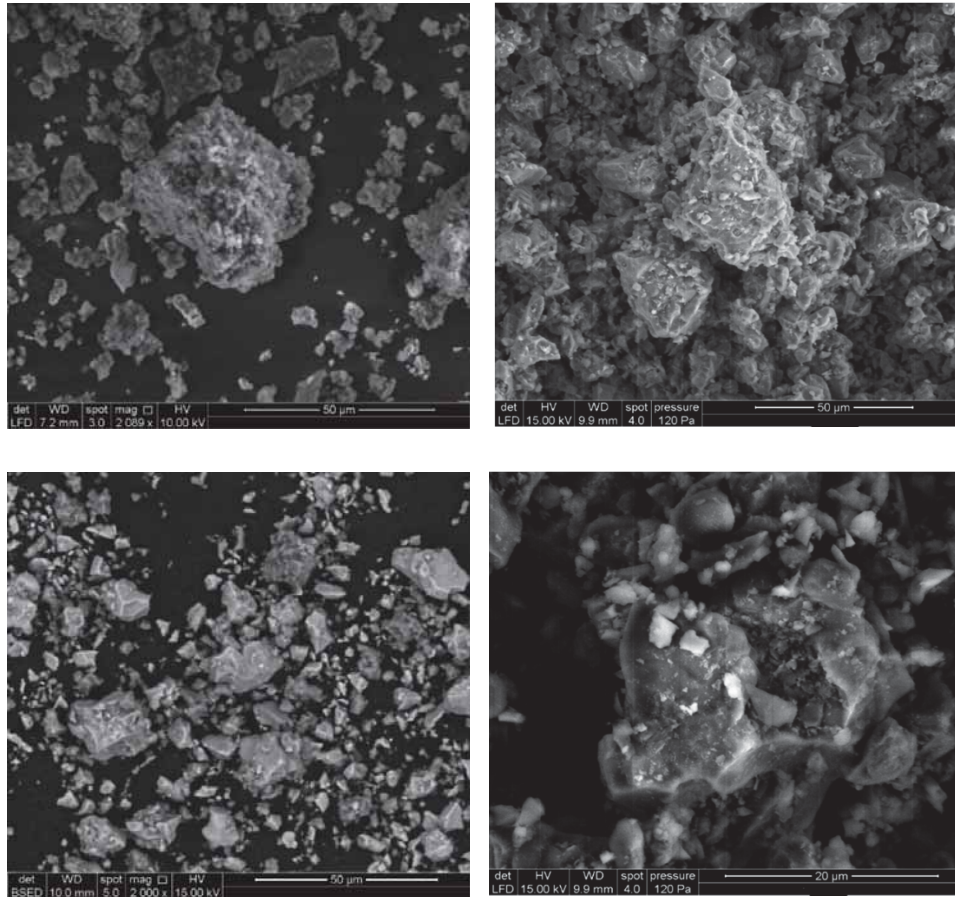


Fig. 5. SEM images of the different powders. Top left: ALS as received (i.e. after fluoride stabilization). Scale bar is 50 µm. Top right: Cement, i.e. ground cement clinker with gypsum. Bottom left and right: Cement with co-ground ALS at two different magnifications: the scale bar on left image is 50 µm, and 20 µm on the right image.



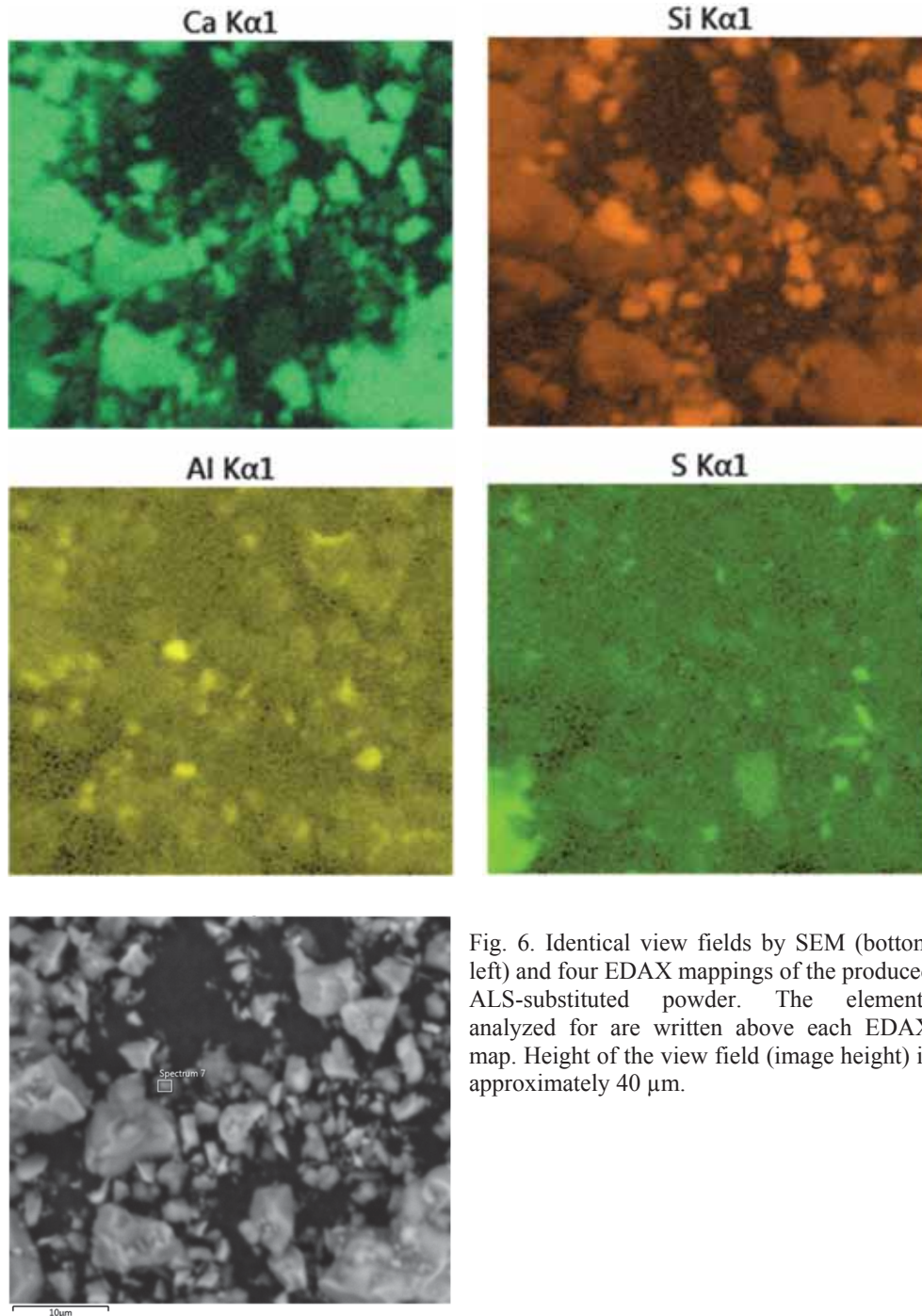


Fig. 6. Identical view fields by SEM (bottom left) and four EDAX mappings of the produced ALS-substituted powder. The elements analyzed for are written above each EDAX map. Height of the view field (image height) is approximately 40 μm.

## 5. Conclusions

The following conclusions can be drawn based on the present laboratory investigation.

1. The fluoride in the ALS seems within the tested regime to be effectively bound as  $\text{CaF}_2$  and does apparently not disturb the cementitious reactions.
2. Co-grinding of ALS and cement clinker (and gypsum) leads to a finer dispersion of ALS in the cementitious system and breaks up ALS agglomerates from about 5-50  $\mu\text{m}$  size to about 1-5  $\mu\text{m}$  size.
3. The inclusion of ALS in the mortar as a mineral admixture with the substitution ratio of 10% of cement mass resulted in a higher air content and a corresponding reduction in the flow compared with the reference mortar. Compared with blending ALS during the mixing, mortar containing co-ground ALS was closer to the reference mortar considering these properties.
4. The addition of ALS did not affect the flexural strength significantly at the investigated hardening times 1 to 122 days.
5. Mortars containing 10% ALS by cement mass exhibited a lower compressive strength compared with the reference mortar. At 28 days the strength reduction is 11% for ALS-substituted, co-ground and 15% for ALS-substituted, blended. Apparently the strength reduction can be accounted for by the increased air content, i.e. it is expected that it by simple means will be possible to incorporate ALS in cementitious systems without strength loss.

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