AMORPHOUS OR CRYSTALLINE

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FLY FLUID ASH

- Specific waste material: Powdered brown coal is burned together with crushed calcite ($CaCO_3$).
- The burning temperature never overcomes the 820°C.
- Temperature of burning decomposes calcite and its most active form lime (CaO) captures all sulfur oxides coming from the burned coal.
- The XRD analyses recognize quartz (SiO_2), remaining calcite, lime (CaO), anhydrite ($CaSO_4$) and hematite (Fe_2O_3).

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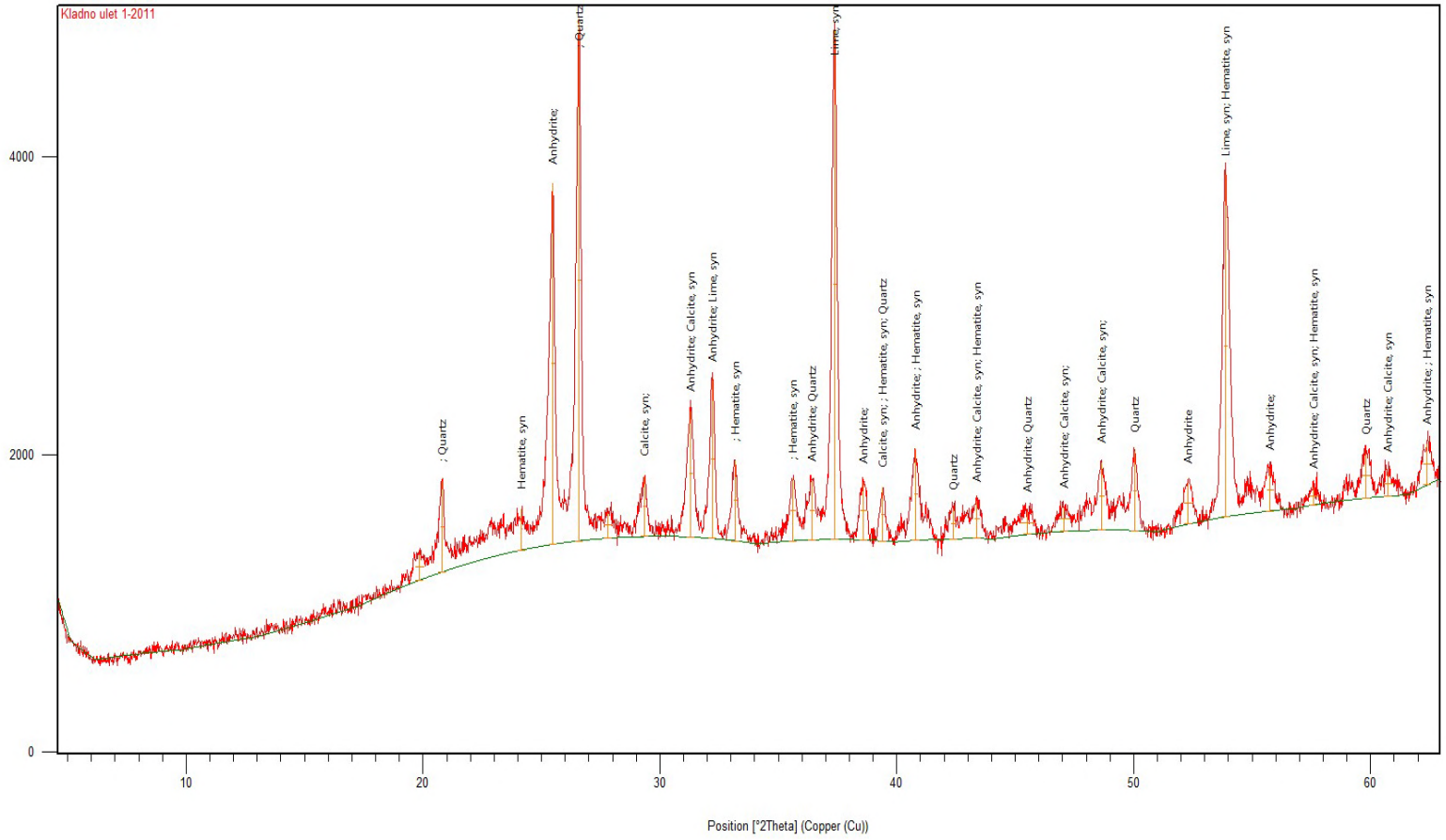
XRD PATTERN OF FLY FLUID ASH



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THE CHEMICAL ANALYSES

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Material /oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3	L.O.I
Fluid Fly Ash	36.01	26.22	5.58	2.25	16.54[a/]	1.75	0.85	<0.11	5.55	4.50 [b/]

[a]/ The content of the "free CaO" (serving as an alkaline activator) is about 10.65 wt. %.
[b]/ The L.O.I. exhibits a loss of the $(OH)^-$ groups and CO_2 from portlandite and calcite, with the unburned carbon content being below 0.2 wt. %.

We could see the discrepancy: The XRD does not identify the alumina-silicates which dominate the chemical composition.

TEMPERATURE OF BURNING

- We have to repeat the fact of relatively low burning temperature – 820 °C.
- The particle of milled coal shortly burns in suspended layer over the grid but long enough that aluminum ion could change its configuration to the oxygen.
- We have to understand that aluminum detected by chemical analyses is always bonded to the silicon, forming alumina-silicates. (In case of ashes – residua of clayed materials).

FLY FLUID ASH - WASTE OR SECONDARY MATERIAL ?

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- ASTM classified these ashes as the C-ashes. (Due to the high amount of calcium containing matters).
- It is difficult or impossible to use these ashes as additives to the cement for their relative high content of CaO, eventually $Ca(OH)_2$ and $CaCO_3$.
- It is of course known that the fresh and watered fly fluid ash hardens relatively quickly due to the supposed reaction of calcium containing oxides and hydrates. This effect is usually explained through the reaction with air carbon dioxide forming finally the calcium carbonate.
- But what about the thermally treated alumino*) - silicates?

*) alumina-silicate is used for the well organized crystal forms and in case of amorphous structure according to the reviewer's of the scientific journals we use above mentioned expression.

NUCLEAR MAGNETIC RESONANCE IN SOLID STATE

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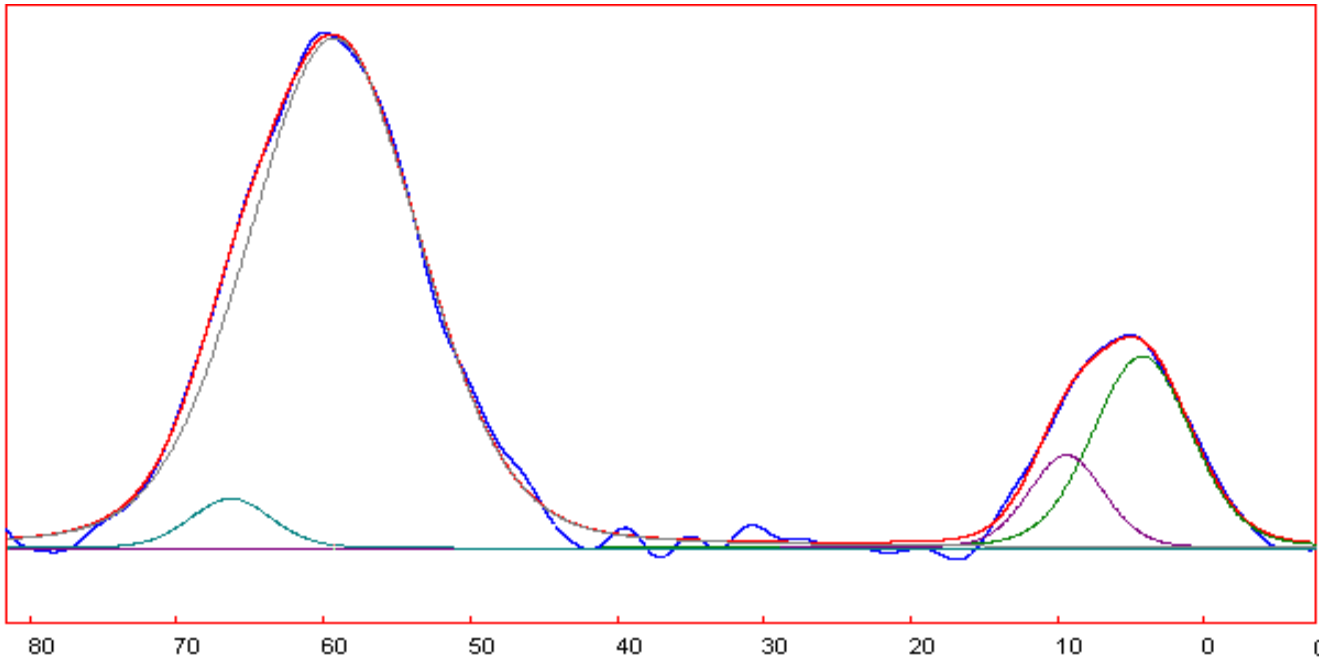
- ^{27}Al Magic Angle Spinning - Nuclear Magnetic Resonance (MAS-NMR) analyses in solid state could identify the coordination of aluminum ion to the oxygen. The pattern shift corresponds to the change from naturally hexa-coordination to the tetra-coordination which reflects the effect of elevated temperature.

- The specific shift from the position close to „0“ ppm [6] Al changes to 58 ppm assigned to the [4] Al (tetra-coordination).

^{27}Al MAS-NMR of the fluid ash



We could observe a typical shift from [6] Al to the dominantly [4] Al coordination which is indispensable for alkalization in aqueous solution.

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THE ACTIVE FLAY ASH PARTICIPANTS

- The XRD analysis shows calcium crystal phases, the MAS-NMR confirms aluminum ion in [4]Al.
- Residual alumino-silicates, in form of $Al_2O_2Si_2O_5$ are generally amorphous (In Czech coal deposits the clayed mineral is kaolin).
- The mixture of lime (CaO) and portlandite ($Ca(OH)_2$) with water in presence of alumino-silicate forms a milieu for the formation of longer or shorter “geopolymer-like” chaining in calcareous surroundings.
- The partial chained structure does not create complete 3D netting which is typical for geopolymerization, but chained structures are spread in calcareous surroundings.

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LABORATORY TESTS

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- The solids obtained through the well milled and watered fluid ash were sufficiently stabile, insoluble in water and presented acceptable compressive strength (22-25 MPa).
- The best solutions were obtained when fluid ash was mixed with quartz sand and pebbles (compressive strength up to 35 Mpa).
- Best mixtures and results were offered for the verification to the semi-industrial plant with a goal to exploit enormous amounts of waste ash.

SEMI-INDUSTRIAL TESTS

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- It is well known that there is a big difference between laboratory and industrial level.
- The previously calculated ratio (ash/water/ sand) varies due to the change of used technology – laboratory casting technology was substituted in industrial plant by the vibro-compacting machine and the smallest batch was 500 kg of the dry components.
- And more we faced comprehensible industrial skepticism to the novelties – the mixture does not contain Portland cement or additional portlandite, but finally opened new field of study.

CONSTRUCTION OF TESTING WALL

- Permanent fear of the brick quality was controlled on constructed small wall built on the concrete basement and left without any protection against the rain or snow – outdoor samples.

- Two bricks were left in ambient conditions inside the installation (we could considered this condition as a dry place – e.g. heated during the winter time). Later named as indoor samples.

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TESTING WALL (70 CM HIGH)

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XRD RESULTS AFTER 18 MONTHS

- Still combating the industrial skepticism we were pressed to verify changes in fabricated items, if any. The outdoor pieces were of course slightly damaged on the contact with a concrete basement due to the lack of the insulation.

- We took some material from the outdoor wall (bottom and wet), and the samples were taken also from the indoor bricks.

- Dried, crushed and carefully milled samples were analyzed by the XRD with surprising results.

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XRD PATTERN OF THE SAMPLE FROM THE OUTDOOR BRICKS

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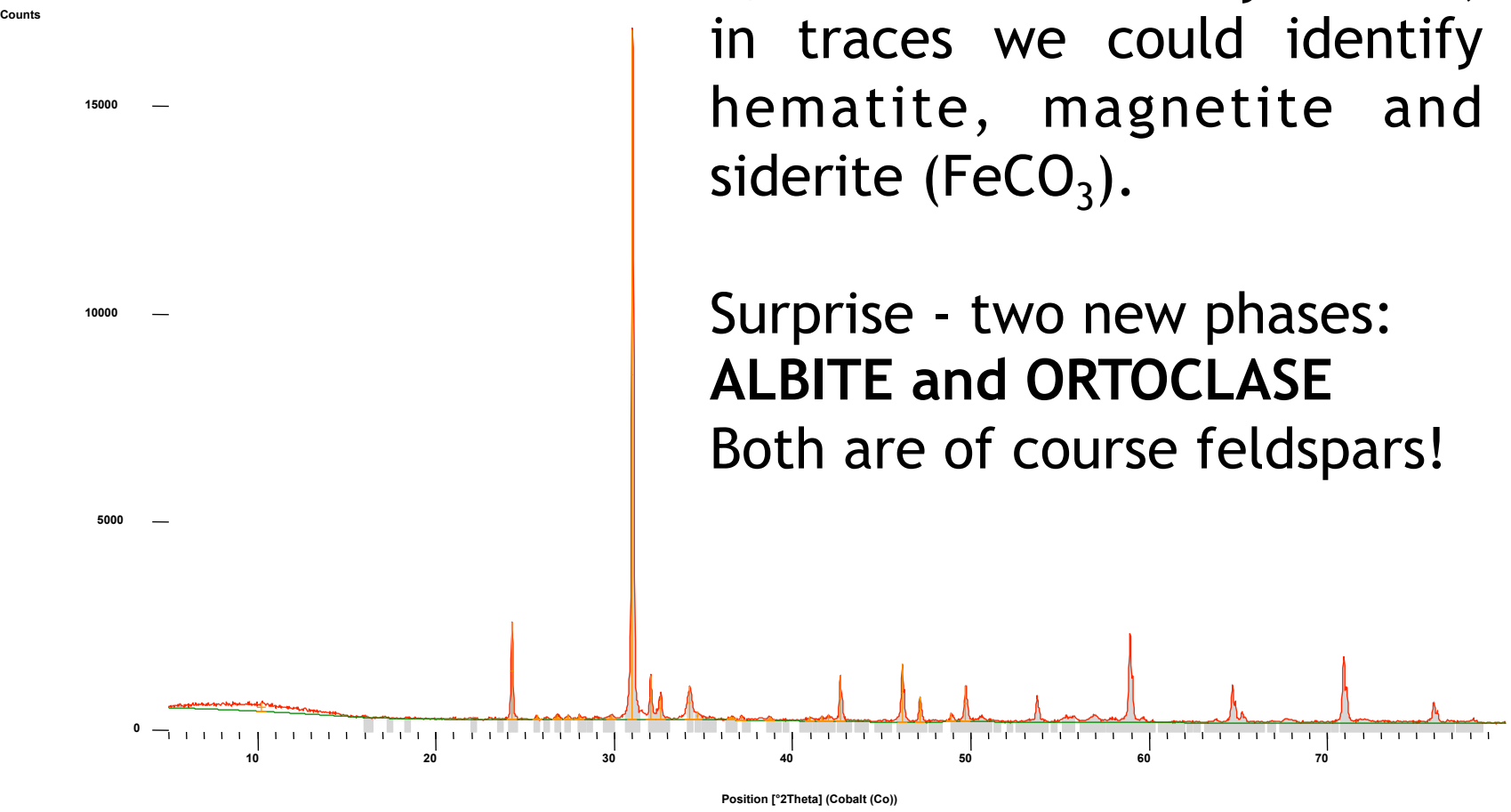

Quartz is followed by calcite, in traces we could identify hematite, magnetite and siderite ($FeCO_3$).

Surprise - two new phases:
ALBITE and ORTOCLASE
Both are of course feldspars!

SIMILARITIES

- It is well known that four coordinated aluminum ion takes part in the crystal structure of feldspars. (Each negative charge of aluminum ion is equilibrated by one positive charge of alkali).
- It is well known that zeolites have also in their structures four coordinated aluminum ion.
- We pretended and proved four coordinated aluminum ion in used fluid ash. Invisible on XRD patterns on the beginning due to its amorphous alumino-silicate structure, but proved by MAS-NMR.
- Now, the XRD discovers newly formed feldspars in calcareous surrounding through the time and effect of water only.

THE INDOOR SAMPLES

- In contrast, the indoor samples kept in dry place and in usual ambient conditions do not present a sign of feldspars and their XRD pattern shows dominant calcite ($CaCO_3$) followed by quartz (SiO_2).

- Next components are melilite ((Ca_2 $Mg_{0.54}$) ($Al_{0.92}Si_{1.54}O_7$)), gypsum ($CaSO_4.2H_2O$) and hematite (Fe_2O_3), but in traces only.
- Both samples have dominant calcite ($CaCO_3$) followed by quartz (SiO_2).
- But XRD shows two different cases: In case of outdoor samples calcite and quartz are completed by feldspars but indoor samples are followed by hardly identifiable traces.

METAMORPHOSIS

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- The metamorphosis of natural minerals is known, but the geologist controlling the XRD analyses of the sampling on one side confirms the feldspars and on the other hand has the doubts about the possible transformation without the effect of temperature.

- We suppose that the only difference is acting water. The porous bodies of the bricks are moisture-absorbing stuff and than water could act as an movable agent for alkalis – the others (alumino-silicates) are ready to form chains or as XRD analyses confirm:

Feldspars

CONTROL AND CONTINUATION

- Because of the continuous cooperation with industry we have built new wall in last autumn and we are going to check the crystal phases and their eventual changes again in next spring.
- We pretend that specific conditions of the separate and probably partially chained precursors could finally terminate in new crystal forms. The surroundings of slowly changed calcareous milieu (water and superficially also CO_2) and open porosity are the basic conditions.
- We have not observed the similar changes in perfect 3D netting of classic geopolymer but some papers mention the observation of crystal zeolites formed through the alkalization of thermally treated clayed minerals.
- We promise to continue the study of the possible metamorphosis.

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Thanks for your attention