Ashes of Oxyfuel- and Air-Fired Pulverised Fuel Combustion Processes – Mineralogical Characterisation and Long-Term Modification

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1 Introduction – Overview of our Current Work

The focus of our work was the mineralogical analysis of ashes obtained from the combustion of soft brown coal (93.4 % huminite, 4.2 % liptinite, 0.8 % inertinite, 1.6 % pyrite and quartz; detectable amounts of Ca, Fe, Na, K, Mg, Al, Si, S, Cl in the macerals) from the open mine site Welzow-Süd in Lower Lusatia (East Germany). The combustion process was achieved in the Atmospheric Pulverized Fuel Combustion Rig (KSVA) of the Institute of Combustion and Power Plant Technology (IFK), formerly Institute of Process Engineering and Power Plant Technology (IVD) at Universität Stuttgart in air and in the oxyfuel mode. Such ashes, which form during the combustion (oxyfuel process) for power production, were characterised with the methods of polarising microscopy, X-ray diffractometry, electron microprobe analysis and carbon/water-analytics and compared with ashes from the conventional combustion process in air.

2 Generation of Ashes in the Atmospheric Pulverised Fuel Combustion Rig

2.1 Introduction to the Applied Oxyfuel Process and Experimental Procedure

There are numerous possibilities for the reduction of greenhouse gases, generated by the production of energy from coal, such as the oxyfuel process (figure 1). In contrast to the ordinary combustion with air, the KSVA is operated with a gas mixture of oxygen with a purity of more than 95 vol.-% and reconducted exhaust gases and, thus, broadly without nitrogen. The oxygen content is raised in the oxyfuel-process to approximately 27 vol.-%. During the recirculation of the exhaust gases, a gas is developed, which consists mainly of CO_2 and water. The CO_2 could be captured and stored directly. [1]

	reference	
	AIR	OXY
power output [kW_{th}]	286	286
O_2 global [vol.-%$_{dry}$]	20.9	32.9
O_2 global [vol.-%$_{humid}$]	20.6	25.9
O_2 exhaust gas [vol.-%$_{dry}$]	2.3	3.7
exhaust gas vol. [m^3 N/h$_{humid}$]	323	233
exhaust gas humidity [vol.-%]	10	21
recirculation rate [%]	–	71
adiabatic flame temperature [°C]	1881	1710

**Table 1:** Test parameters/gaseous atmosphere, air/oxyfuel in the KSVA.

In the conventional power station operation with air and without exhaust gas recirculation the concentration of CO_2 in the less CO_2-rich exhaust gas must be increased by air stripping with ammonia (NH_3), which is a relatively expensive process. [2] [3]

The ashes investigated in this paper were generated in the KSVA, an experimental power plant, in air and in the oxyfuel mode (table 1). The maximal thermal output of the KSVA is 500 kW. The Vattenfall 30 MW oxyfuel experimental power plant situated at Jänschwalde (East Germany) is operated similarly as the KSVA. Differing in size, the Jänschwalde power plant has to be fired laterally and uses an air fractionation unit and not gases from storage tanks like the KSVA that is fired from the top.

The KSVA (figure 1) consists of a vertical combustion chamber with a roof burner. The combustion chamber has an internal diameter of 0.85 m and consists of six ring-shaped elements with a length of 7 m. The upper four cylindric parts consist of refractory material with a thickness between 100 und 140 mm. The combustion chamber has a water cooling system at the outside. The cooling water flows through every single combustion chamber element from bottom to top. In the upper part is the burner, a flame failure controller and a gas burner for heating up the device. Combustion chamber pressure, combustion air flow and temperature and cooling water temperature are adjustable.

The KSVA was extended for oxyfuel operation. Tubes for carbon dioxide and oxygen were installed to supplement the existing power plant consisting of coal feeding, burner, combustion chamber, air preheater (AP), electrical precipitator (EP) 1 to 3, fan 1 and stack. No air fractionation unit exists. Instead, carbon dioxide and oxygen are provided via storage tanks. Another speciality is the recirculation unit for the exhaust gases, which are transported after cleaning into the EPs via fan 2 back to the burner. The recirculation rate is alterable. Fan 1 is responsible for the transport of gases through the system by pulling them in direction of the stack as the flue itself is not strong enough to do so. In addition, fan 1 is used to control the flame. The maximum temperatures, burning brown coal, were up to 1300°C, when in full load up to 50 kg coal per hour is burned. Higher temperatures would cause overheating problems. The temperatures in the lower part of the combustion chamber should not be significantly higher than 700°C to prevent damage of the EP which is designed for a maximum of 250°C only.

For operation in air mode the recirculation of the exhaust gases is turned off and, instead, air is ingested through valves as shown in figure 1. The air is both led through the AP and used for coal feeding.
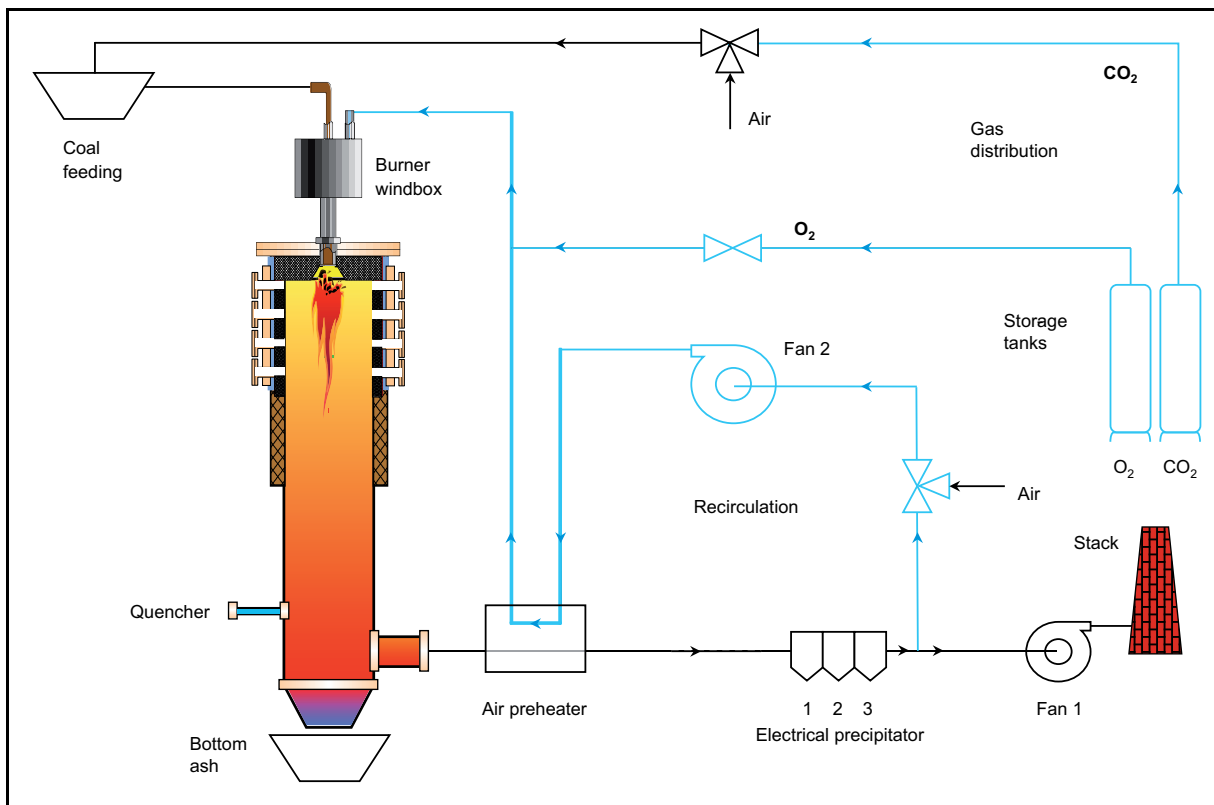
Figure 1: Schematic construction of the KSVA. Equipment drawn in blue colour marks the extensions added for oxyfuel operation.

2.2   Comparison of Ashes Generated in the KSVA in Air and in Oxyfuel Mode

The experimental products of the combustion in the KSVA are composed of crystalline and vitreous constituents. The latter are typically present in spherical shape. Thereby, it is difficult to detect the amount of glass.

Analyses of the crystalline constituents of all ashes from the AP using X-ray diffractometry show an identical mineral compound with only small differences of peak height of some phases given in table 2. The analyses of the ashes from the EP also show a broadly identical mineral compound whereas only the quantity of anhydrite differs from the oxyfuel samples. The quantity of hematite could not be well determined because of a peak overlay with brownmillerite.

sample description	aluminium hydroxide $Al(OH)_3$	anhydrite $CaSO_4$	brownmillerite $Ca_2(Fe_{1,52}Al_{0,48})O_5$	hematite Fe_2O_3	calcium oxide CaO	magnetite Fe_3O_4	merwinite $Ca_3Mg(SiO_4)_2$	periclase MgO	quartz SiO_2
LA-TBK AP AIR	++(+)	+++++	++++	++	++	+	indet.	++(+)	++++
LA-TBK AP OXY	+	++++	++++	++	++	+	indet.	++(+)	+++++
LA-TBK EP AIR 1		++++	++++(+)	+++	++	+(+)	indet.	+++(+)	++
LA-TBK EP OXY		+++++	++++(+)	+++	++	+(+)	indet.	+++(+)	++
LA-TBK EP AIR 2		++++(+)	+++++	indet.	++	+(+)	indet.	+++(+)	++

Table 2: Synopsis of five representative samples taken from the air preheater (AP) and the electrical precipitator (EP) of the KSVA; air and oxyfuel. Semiquantitative phase identification using Cu-Kα-radiation, 40 kV, 40 mA. + very little, ++ little, +++ medium, ++++ much, +++++ very much.

All studied ashes from the AP and EP contain anhydrite, brownmillerite, calcium oxide, magnetite, periclase and quartz. Nonetheless, aluminium hydroxide was only found in the AP. The largest difference in the intensity of an X-ray reflection is related to quartz. The main body of quartz is already filtered out of the exhaust gas in the AP, so that only some quartz is able to reach the EP.

The comparison of ashes generated in air and in oxyfuel mode, taken from the AP, show that they do not differ from each other even though the quantity of some minerals alternate in a minimal range not depending on air or oxyfuel mode in analogy to the ashes taken from the EP. As mentioned above, aluminium hydroxide is only found in the AP. Nevertheless, the quantity of Al in the ashes of the EP is assumed to be the same quantity as in the AP due to the fact that ashes from the EP consist of much more brownmillerite ($Ca_2(Fe_{1,52}Al_{0,48})O_5$) than ashes from the AP.

Ashes from the AP and EP show a clear difference in size of the ash particles which reach a diameter of more than 100 μm in the AP and up to 50 μm in the EP. The main body of the AP and EP ashes is as small as 25 μm and 2 μm, respectively. Although the particle shapes can differ from the place of sampling most particles are spherical; square-cut particles can also be found, but almost exclusively in the ashes from the AP. This is explained by the fact that a smaller particle, due to its larger surface relative to its volume, melts more easily.

3 Long-Term Exposure of Ashes in Air- and Oxyfuel-Atmosphere

3.1 Experimental Procedure

	CO_2	H_2O	N_2	O_2	SO_2
Air	17.0 vol.-%	68.5 vol.-%	10.0 vol.-%	4.0 vol.-%	0.5 vol.-%
Oxyfuel	74.5 vol.-%	20.0 vol.-%		4.0 vol.-%	1.5 vol.-%

Table 3: Air and oxyfuel atmosphere parameters in the laboratory tube furnaces used for the long-term exposure experiments.

Experiments were achieved with parts of different heat exchanger pipes stored in circa 4 cm long and 2 cm wide ceramic shuttles. The remaining volume up to the upper edge of the shuttles was filled up with ash. The shuttles were moved into pre-heated laboratory tube furnaces for a period of up to 350 hours under air and oxyfuel atmosphere (table 3) and temperatures of 670 and 770°C.

The ash used for the experiments was generated in the KSVA in air mode and taken from the EP. For this type of experiment it was important to use an ash with amounts of coke as small as possible. Reactions of ashes with unburned coke during the experiments could thereby be prevented. This essential criterion cannot be achieved in oxyfuel mode because the flame often goes out while coal is still transported to the burner. The results of the analysis of ash before the long-term exposure experiments are reported in table 2: "LA-TBK EP AIR 2".

3.2 Macroscopic Characterisation

The samples in figure 2 were treated as described in table 4. In summary, there are no macroscopic differences detectable between ashes, which were stored in the furnace for the same time and temperature. Also no differences between ashes stored in air and oxyfuel atmosphere were noted.


Figure 2: From left to right: LA-TBK EP 100 670 AIR, LA-TBK EP 350 670 OXY, LA-TBK EP 100 770 OXY, LA-TBK EP AIR 2.

3.3 Light-Optical Microscopic Analysis

Figures 3a to 3d show four selected ashes, which were examined as described in table 4. Samples treated at 670°C with both air and oxyfuel, typically showed an intensive red tone even after the shortest time in the furnace of 95 h. Originally, the starting ashes were light-coloured.

The samples, which were in the furnace at 770°C, were always light-coloured independent of the experimental duration and gas atmosphere.
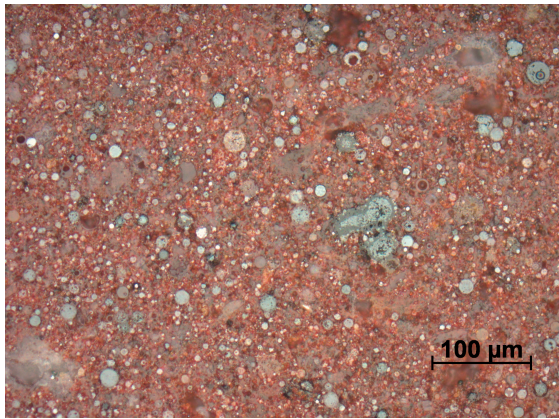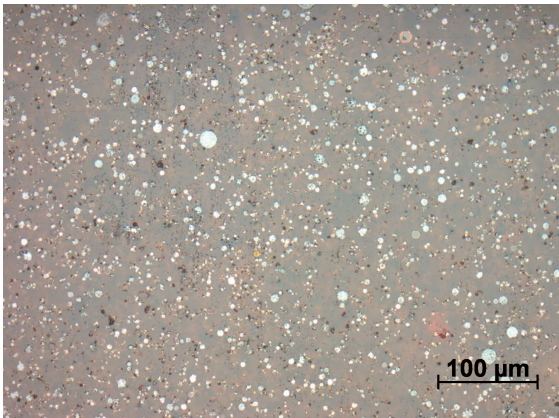
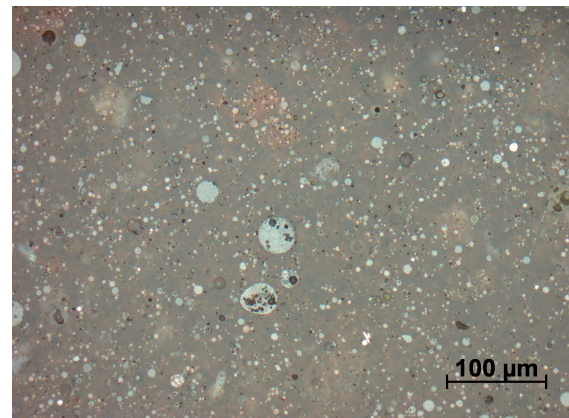**Figure 3a: LA-TBK EP 100 670 AIR.** Reflected light, 20x magnification.
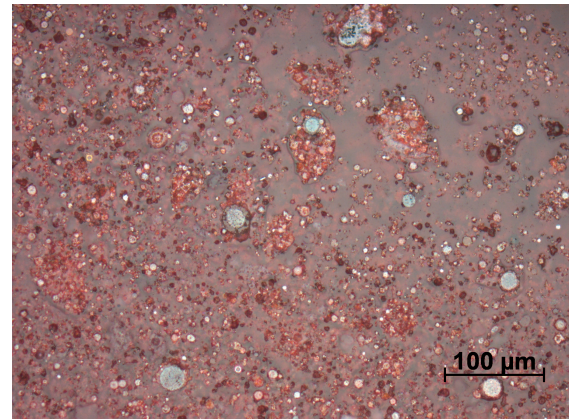
Figure 3b: LA-TBK EP 350 670 OXY. Reflected light, 20x magnification.

The red colour of the matrix surrounding the light-coloured particles results from hematite.

Figure 3c: LA-TBK EP 100 770 AIR. Reflected light, 20x magnification.

Figure 3d: LA-TBK EP 100 770 OXY. Reflected light, 20x magnification.

Because of lacking hematite the matrix surrounding the ash particles remained light-coloured.

3.4   X-Ray Diffraction Analysis

Analyses of the ashes, which were exposed at 670°C, using X-ray diffractometry yielded an identical mineral compound with only small differences of the peak heights of some phases (table 4). Thus for example, the content of aluminium hydroxide ($Al(OH)_3$) slightly increased with experimental duration. The peak height of merwinite could not be well determined because of a peak overlay with brownmillerite and hematite.

Similarly, the ashes, which were treated at 770°C for 100 h in both air and oxyfuel, consisted of an identical mineral compound with only small differences in the peak height of quartz.
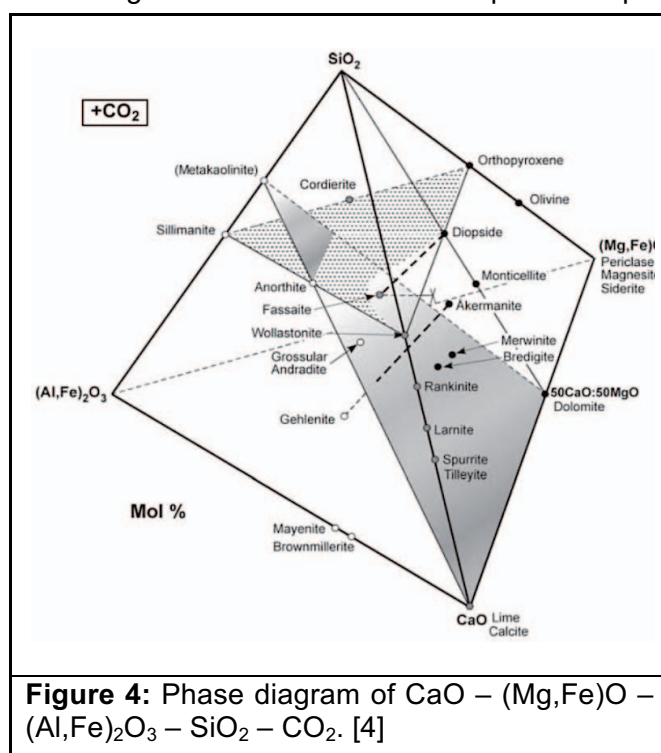
Comparing the ashes stored at 670°C and 770°C, it is recognisable that aluminium hydroxide, anhydrite, calcium oxide, periclase and quartz exist in all ashes. In the ashes exposed at 770°C there is no hematite present but magnetite. Also the magnesite is gone in these ashes.

sample description	exposure period [h]	temperature [°C]	Al(OH)₃ aluminuim hydroxide	CaSO₄ anhydrite	Ca₂(Fe₁.₅₂Al₀.₄₈)O₅ brownmillerite	Fe₂O₃ hematite	CaO calcium oxide	CaCO₃ magnesite	Fe₃O₄ magnetite	Ca₃Mg(SiO₄)₂ merwinite	MgO periclase	SiO₂ quartz
LA-TBK EP 95 670 AIR	95	670	++	+++++		++	+	+		indet.	+	++
LA-TBK EP 100 670 AIR	100	670	++(+)	+++++		++	+	+(+)		+	+	+(+)
LA-TBK EP 202 670 AIR	202	670	+++	+++++		++	+	++		indet.	+	++
LA-TBK EP 250 670 OXY	250	670	+++	+++++		++	+	++		+	+	++
LA-TBK EP 350 670 OXY	350	670	+++	+++++		++	+	++		+	+	+
LA-TBK EP 100 770 AIR	100	770	+	+++++	+++(+)		+		++		+++(+)	+(+)
LA-TBK EP 100 770 OXY	100	770	+	+++++	+++(+)		+		++		+++(+)	++

Table 4: Synopsis of seven representative samples; 95 to 350 h, 670 and 770°C, air and oxyfuel. Semiquantitative phase analysis with Cu-Kα-radiation, 40 kV, 40 mA. + very little, ++ little, +++ medium, ++++ much, +++++ very much.

3.5   Further Findings and Conclusion

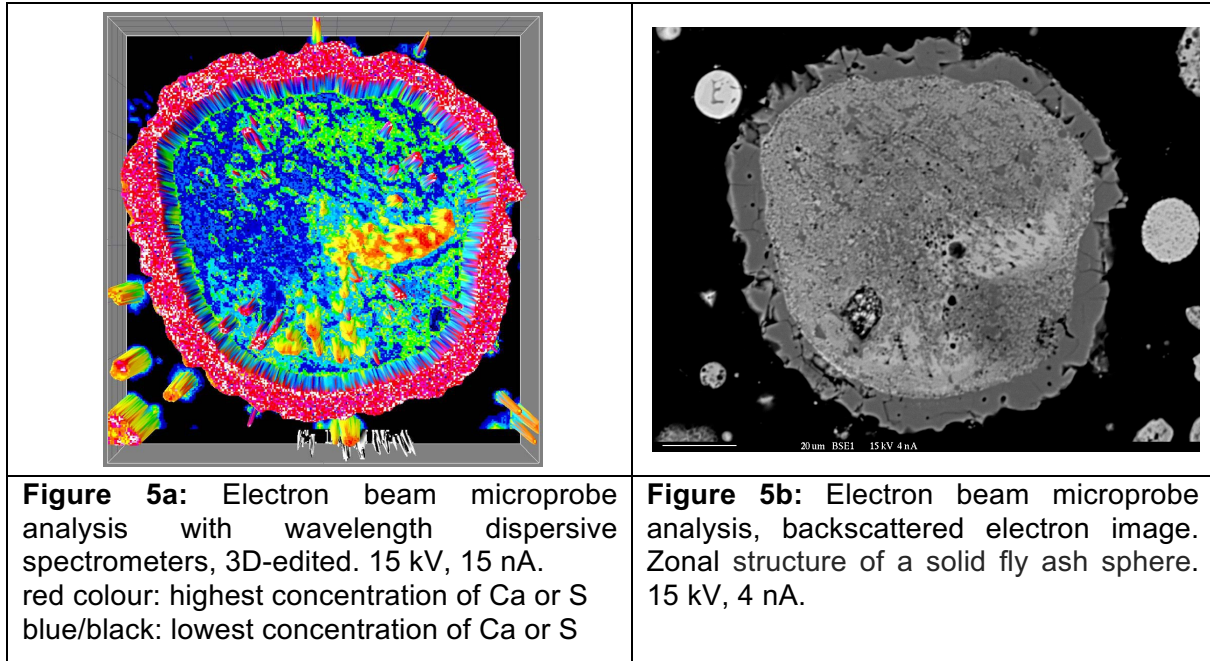In the original ashes used for the exposure experiments, the quantity of hematite could not be well identified because of a peak overlay with brownmillerite. In the ashes exposed at 670°C significant amounts of hematite could be detected applying X-ray diffractometry. More noticeable is the solidification of the ash that can be recognised already after a storage time of 95 h in the furnace. This solidification increases up to 350 h, however, only slightly. If one compares the ashes stored at 670°C and 770°C, independently of air and oxyfuel atmosphere, it is obvious that the latter did not solidify and that the colour did not change to red according to the microscopic examination under reflected light. The ashes seem to have macroscopically only slightly changed in colour tone. The mineral compound must have been altered because aluminium hydroxide is now detectable. In addition, the amount of brownmillerite in the starting material was higher.

Figure 4: Phase diagram of CaO – (Mg,Fe)O – (Al,Fe)₂O₃ – SiO₂ – CO₂. [4]

For the solidification of the ashes, anhydrite is made responsible for (figures 5a and 5b). As a consequence, the solidification via a coating or cement of anhydrite is possible at a temperature of 670°C, whereas at a temperature of 770°C it is not. At 770°C, no difference was recognised compared to the starting material, where the particles only had a thin coating of anhydrite, which already condensated on the particles in the exhaust gas.

Merwinite exists only in the starting material and in the ashes exposed at 670°C. The quantity of periclase is lower if there is merwinite. In the absence of merwinite there is no

hematite but magnetite. These results lead to the conclusion that transformations between brownmillerite and merwinite occurred (figure 4).

The general conclusion from the results of the exposure experiments is that higher temperatures in the brown coal power plant will lead to less adhesion of the ashes on the heat exchanger pipes allowing an increase of efficiency.
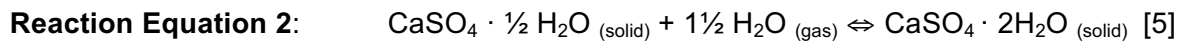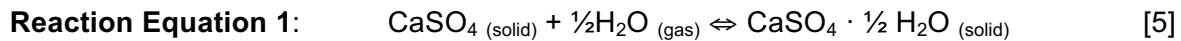

| **Figure 5a:** Electron beam microprobe analysis with wavelength dispersive spectrometers, 3D-edited. 15 kV, 15 nA. red colour: highest concentration of Ca or S blue/black: lowest concentration of Ca or S | **Figure 5b:** Electron beam microprobe analysis, backscattered electron image. Zonal structure of a solid fly ash sphere. 15 kV, 4 nA. |

4 Long-Term Modification in Ambient Atmosphere

| sample description	storage period	$Al(OH)_3$ aluminium hydroxide	$CaSO_4$ anhydrite	$CaSO_4 \cdot \frac{1}{2}H_2O$ bassanite	CaO calcium oxide	$CaSO_4 \cdot 2H_2O$ gypsum	Fe_2O_3 hematite	$MgSO_4 \cdot 6H_2O$ hexahydrite	$MgCO_3$ magnesite	$Ca_3Mg(SiO_4)_2$ merwinite	Ca-Mg-Al-silicate	MgO periclase	SiO_2 quartz
LA-TBK EP 202 670 AIR	0 days	+++	+++++		+		++		++	indet.		+	++
LA-TBK EP 202 670 AIR	10 days		+++++	++			++	+++			indet.		++
LA-TBK EP 202 670 AIR	13 days		+++++	++			++	+++			indet.		++
LA-TBK EP 202 670 AIR	34 days		+++++	++		+	++	+++			indet.		++
LA-TBK EP 202 670 AIR	4 months		+++++	+		+	++	+++			indet.		++
LA-TBK EP 202 670 AIR	6 months		+++++	+		+(+)	++	+++			indet.		++
LA-TBK EP 202 670 AIR	22 months		+++++	(+)		+(+)	++	+++			indet.		++

Table 5: Synopsis of several semiquantitative phase analyses of ash stored in ambient atmosphere for a time period of almost two years. Cu-Kα-radiation, 40 kV, 40 mA. + very little, ++ little, +++ medium, ++++ much, +++++ very much.

Analyses of ashes before storage in ambient atmosphere using X-ray diffractometry yielded aluminium hydroxide. After ten days no aluminium hydroxide could be detected anymore, likewise calcium oxide, periclase, magnesite and merwinite (table 5). The following phases had crystallised in the meantime: bassanite, hexahydrite and probably Ca-Mg-Al-silicates. The exact quantity of these silicates could not be determined because of the poor intensities of these newly formed phases.

As the quantity of bassanite decreases, the quantity of gypsum increases. According to the reaction equations 1 and 2 the transformation from anhydrite to gypsum via bassanite in relatively dry environments is possible:

Reaction Equation 1: $CaSO_4 \text{ (solid)} + \frac{1}{2}H_2O \text{ (gas)} \Leftrightarrow CaSO_4 \cdot \frac{1}{2} H_2O \text{ (solid)}$ [5]

Reaction Equation 2: $CaSO_4 \cdot \frac{1}{2} H_2O \text{ (solid)} + 1\frac{1}{2} H_2O \text{ (gas)} \Leftrightarrow CaSO_4 \cdot 2H_2O \text{ (solid)}$ [5]

According to reaction equation 3, gypsum also directly results from the transformation of anhydrite on or close to the earth's surface, contact with groundwater or surface water provided, according to the following reaction equation:

Reaction Equation 3: $CaSO_4 \text{ (solid)} + 2 H_2O \text{ (liquid)} \Leftrightarrow CaSO_4 \cdot 2 H_2O \text{ (solid)}$ [5]
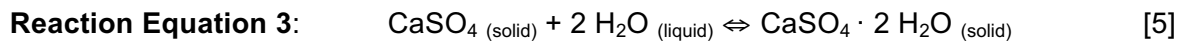
With lacking water the chemical reactions, according to the reaction equations 1 and 2, take place.

The increase of gypsum after approximately one month points to a transformation of bassanite, which decreases according to the X-ray diffraction pattern after four months. Between the first and the fourth months, the anhydrite quantity slightly decreased, which points after the reaction equations 1 and 2 to a transformation into gypsum.

The formation of Ca-Mg-Al-silicates can be explained by a reaction of aluminium hydroxide with SiO_2 and calcium oxide.

The magnesium of the hexahydrite could stem from the decay of periclase, which has been observed in the educts.

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