Geopolymer Formation via Metaclays and using Ferrihydrite

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GeopolymerCamp 2010

Outlook

1. Introduction:
   Two-step procedure for generation of inorganic networks

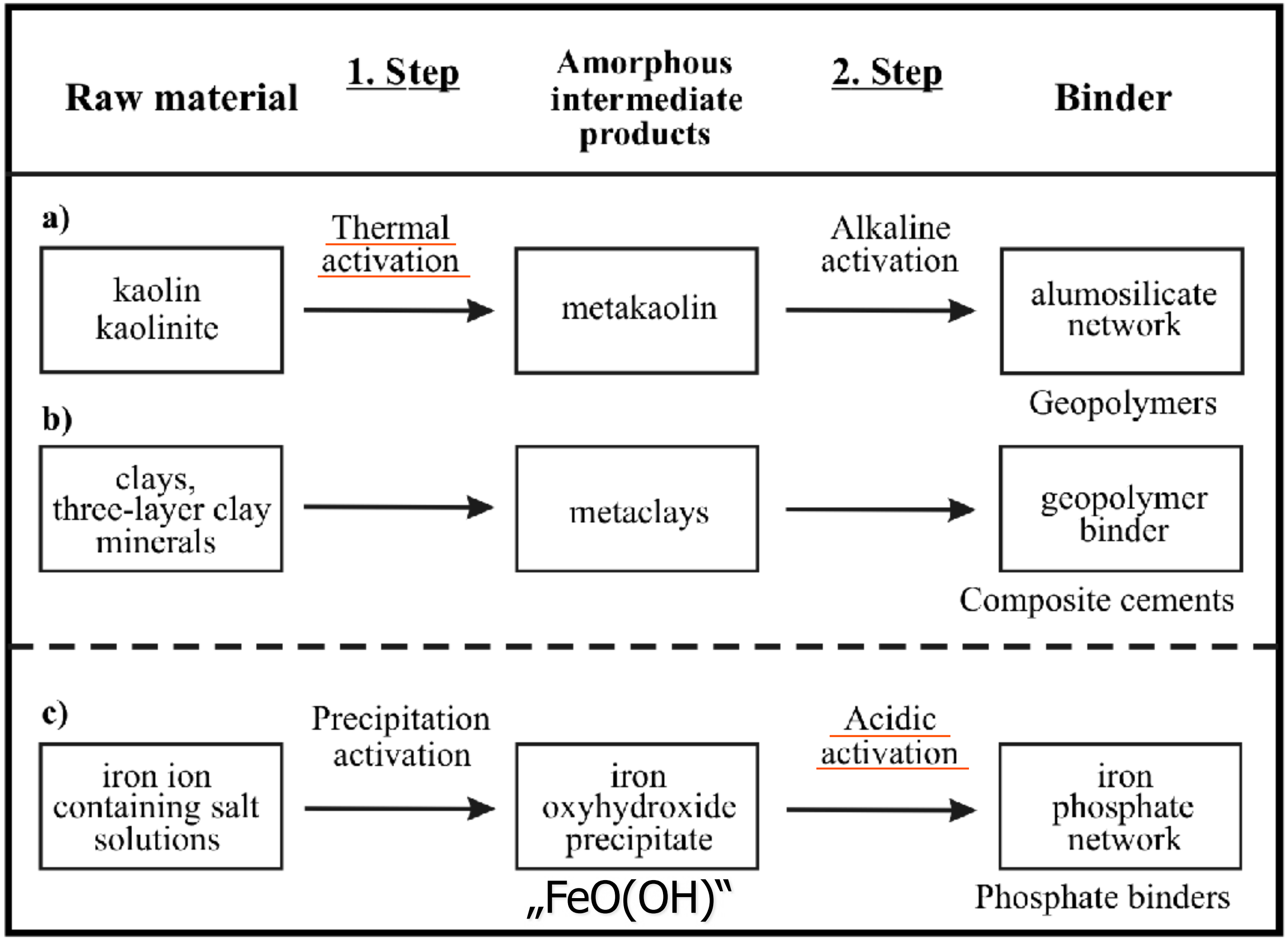
3. Metaclays for geopolymer cements

5. Iron-phosphate network binder using Ferrihydrite (“FeO(OH”)

6. Summary and Conclusions

Bauhaus- University („Van de Velde-Bau“) Main Building

Generation of inorganic networks



Outlook: 2

Outlook: 3

Raw material and thermal activation

Smectitic/illitic clay Ndh, Nordhausen (Germany)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	
Content	64.8	13.7	4.9	1.0	2.6	4.0	0.2	not de-tectable	wt.%

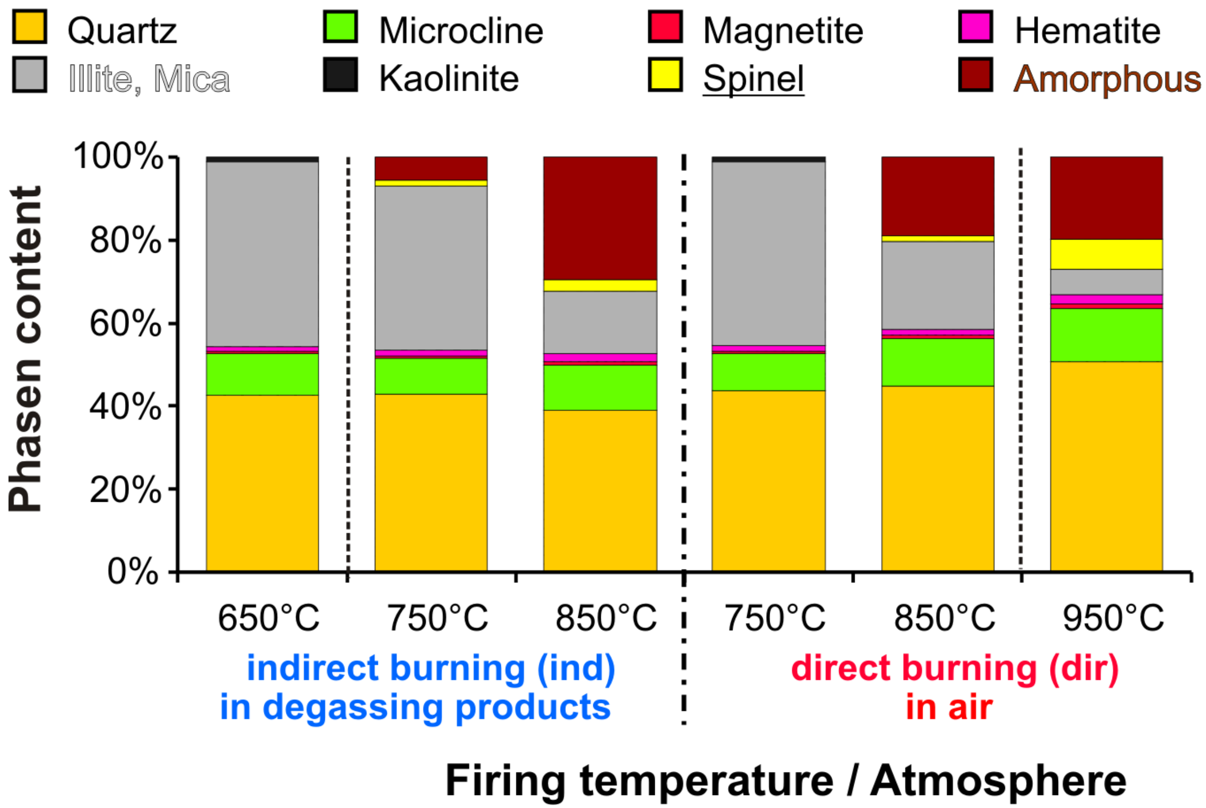
Three-layer-minerals: about 58 wt.%

Estimated molar Si/Al ratio: 3.5(total, including quartz), 1.7(only three-layer clay minerals with assumed Si/Al substitution) and 1.1(all clay minerals)

Conditions of the thermal activation

Temperature procedure	Heating rate: 200 K/h Firing temperatures (1 h): 650, 750, 850 and 950°C Cooling: in the furnace, without electronic control
Gas atmosphere over the clay	Direct burning: in air, open (dry, oxidizing) Indirect burning: in degassing atmosphere, encapsu-lated(wet, reducing)

Phase compositions of the metaclays



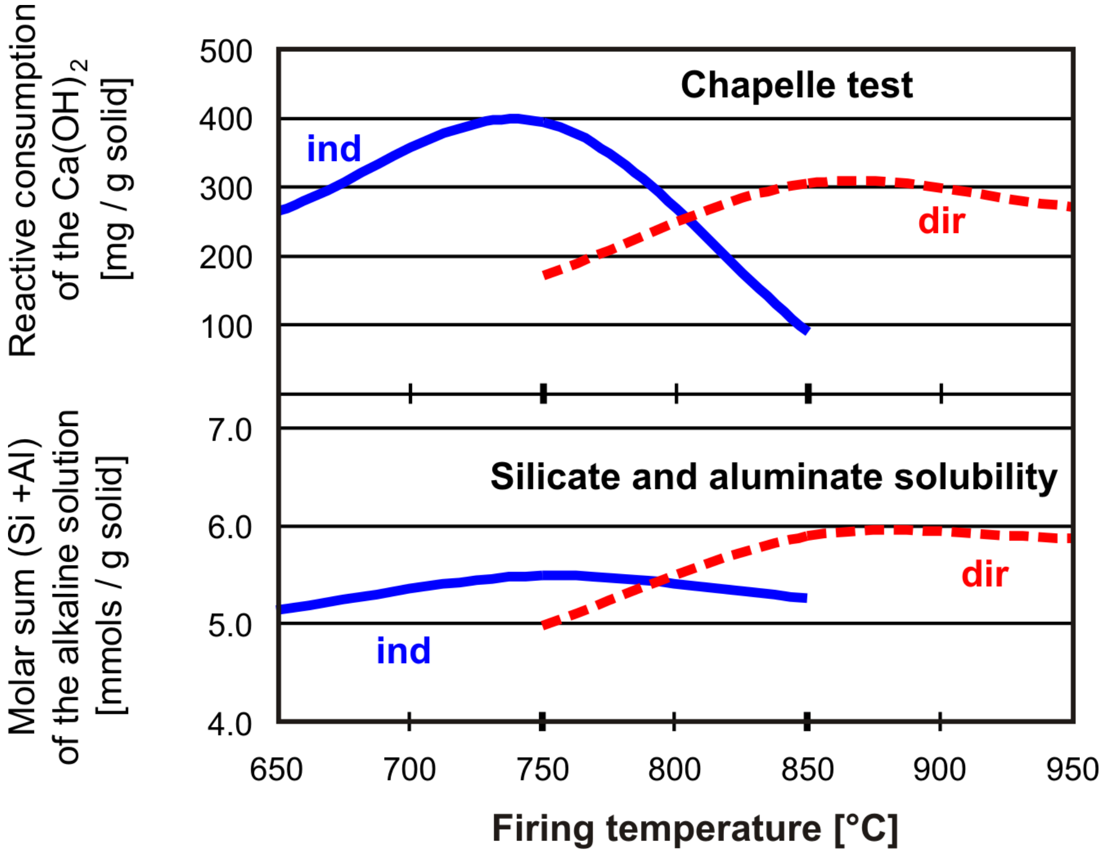
breakdown of three-layer minerals and increasing content of amorphous components

Start of amorphization:

at 750°C (ind)

at 850°C (dir)

Comparison of the Chapelle test and the summary (Si+Al) solubility



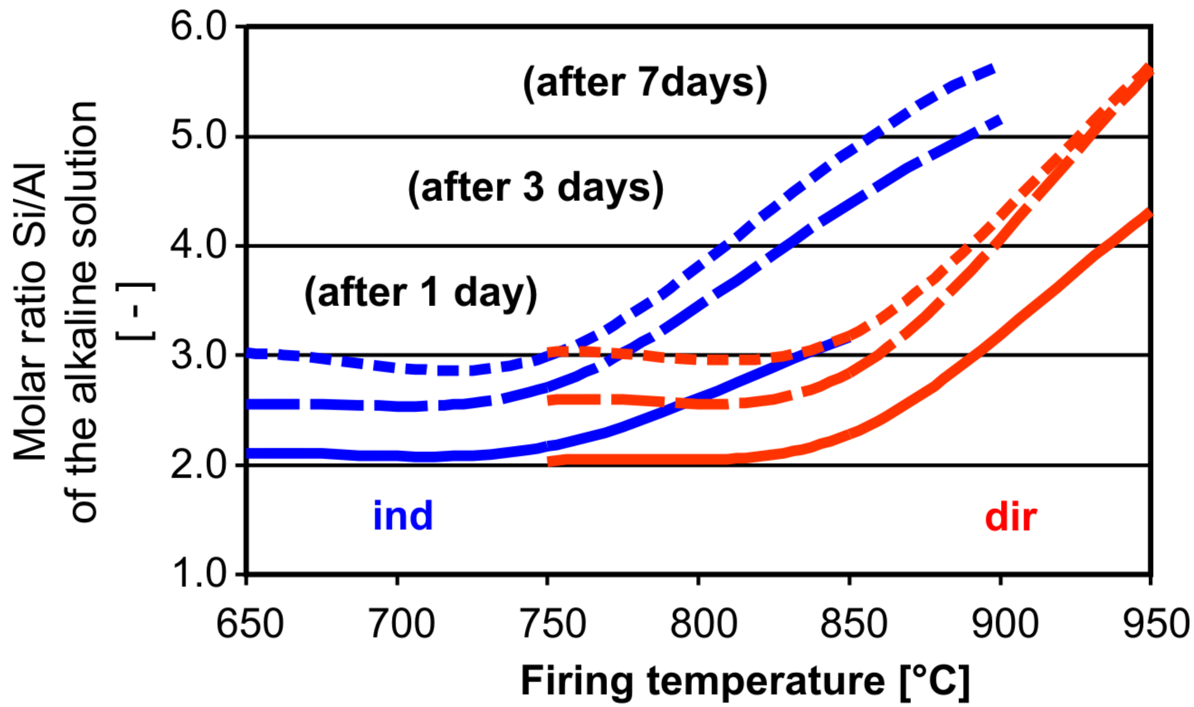
correspondence of the both methods

maximum values of activity:

at 750°C (ind)

at 850°C (dir)

Evolution of the molar ratio Si/Al in the alkaline solution of the metaclays



after 7 days:

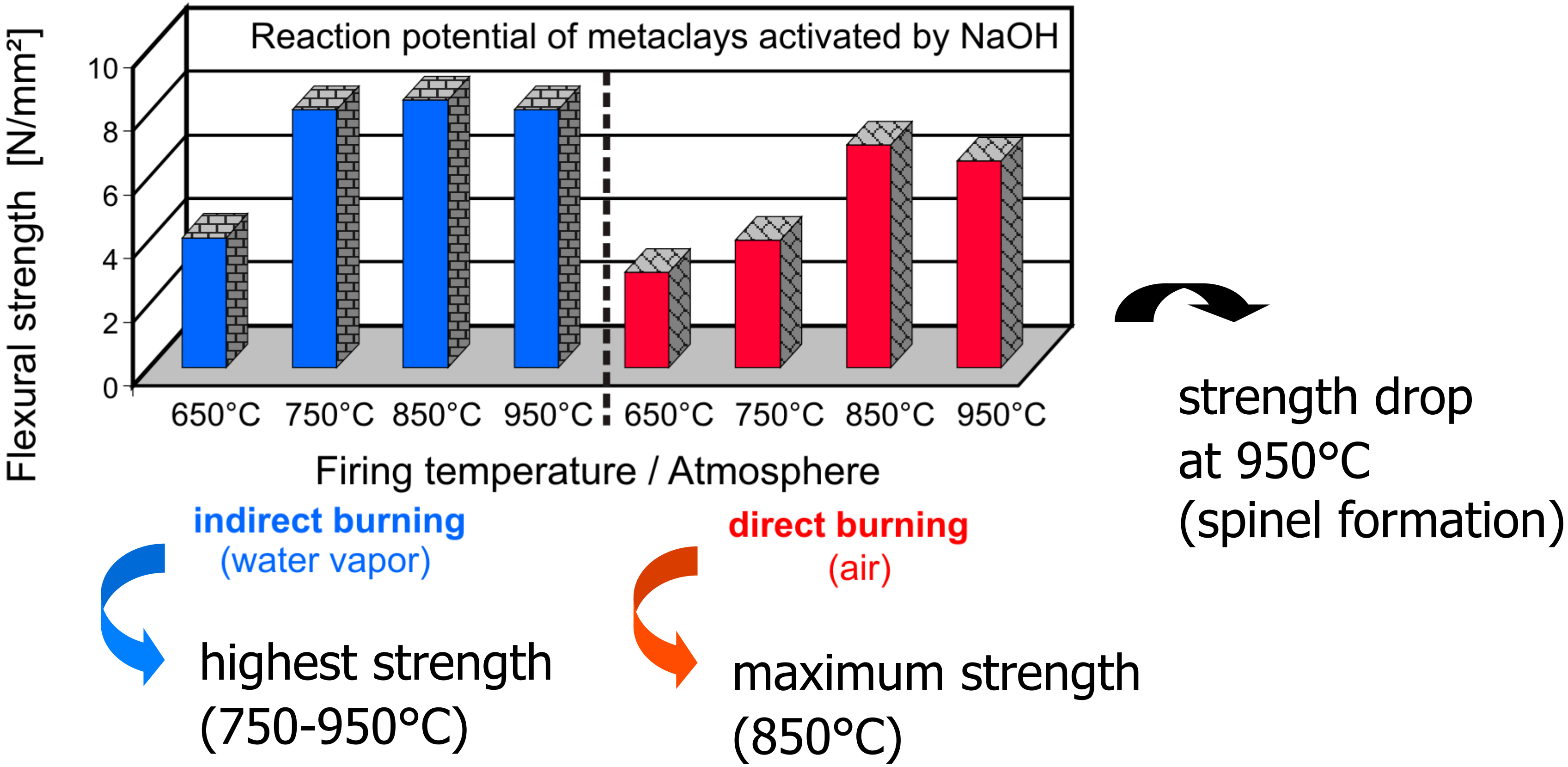
2.2 < Si/Al < 3.0
(750°C, ind)

2.3 < Si/Al < 3.2
(850°C, dir)

Si/Al > 3.5 !

at higher temperatures

Influence of burning conditions on the strength of the binders – alkali-activated metaclays (90d, 75% r.h., 20°C)



Preparation of iron-phosphate networks

Hypothesis: Condensation steps

$$(HO)_2Fe\text{-}OH + HO\text{-}PO(OH)_2 \rightarrow (HO)_2Fe\text{-}O\text{-}PO(OH)_2 + H_2O$$

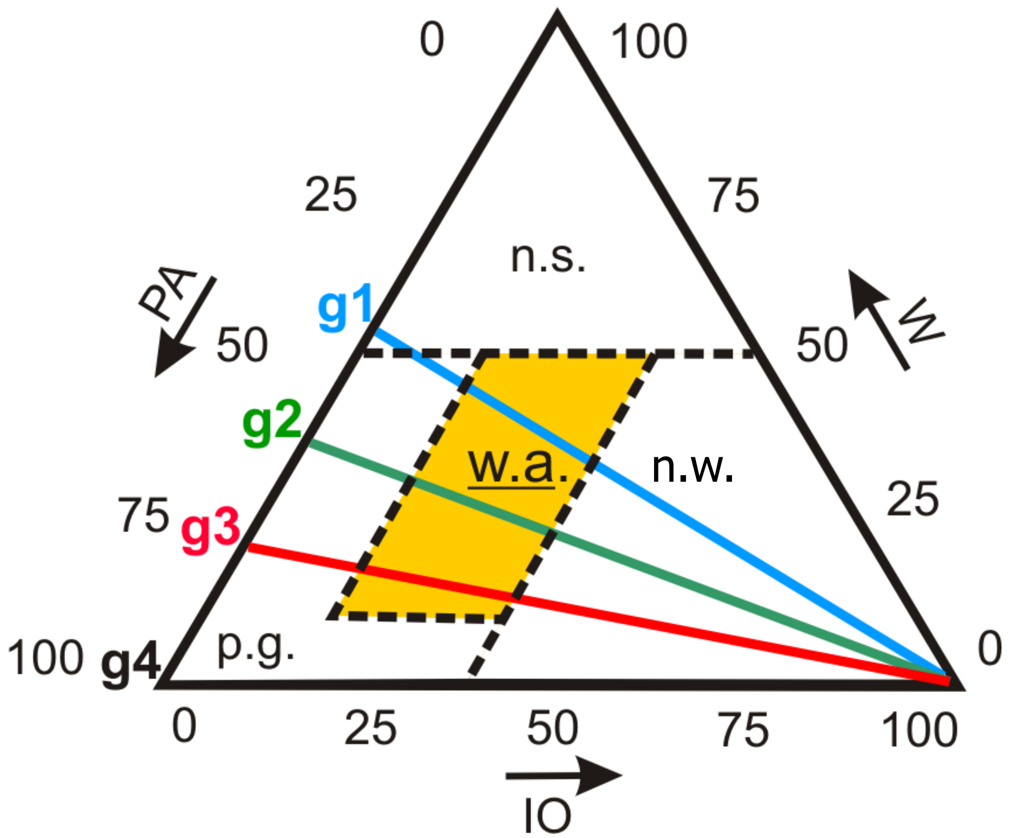
Raw materials and characteristic of the iron oxyhydroxide

Mineral phases of IO:	**amorphous Ferrihydrite (“FeO(OH)”, ≳ 55 wt.%)** **Calcite (cryst. $CaCO_3$, ≈ 10 wt.%)**

Analized compo-nents of IO	**Fe_2O_3**	**CaO**	**SiO_2**	**MnO**	**P_2O_5**	**MgO**	**Al_2O_3**	**Na_2O**	**K_2O**	**TiO_2**
[wt.%]	**71.3**	**10.0**	**14.5**	**1.5**	**1.4**	**0.7**	**0.3**	**0.2**	**0.03**	**0.01**

Iron-oxyhydroxide, IO	**technical residual product, amorphous (XRD)**
Phosphoric acid; PA	**H_3PO_4, cons. (85%), p.a.**
Water, W	**H_2O, deionised water**

Working area in the system
Iron oxyhydroxid (IO) - Phosphoric acid (PA) - Water (W)

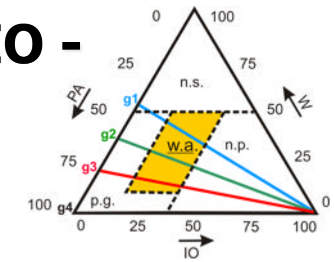


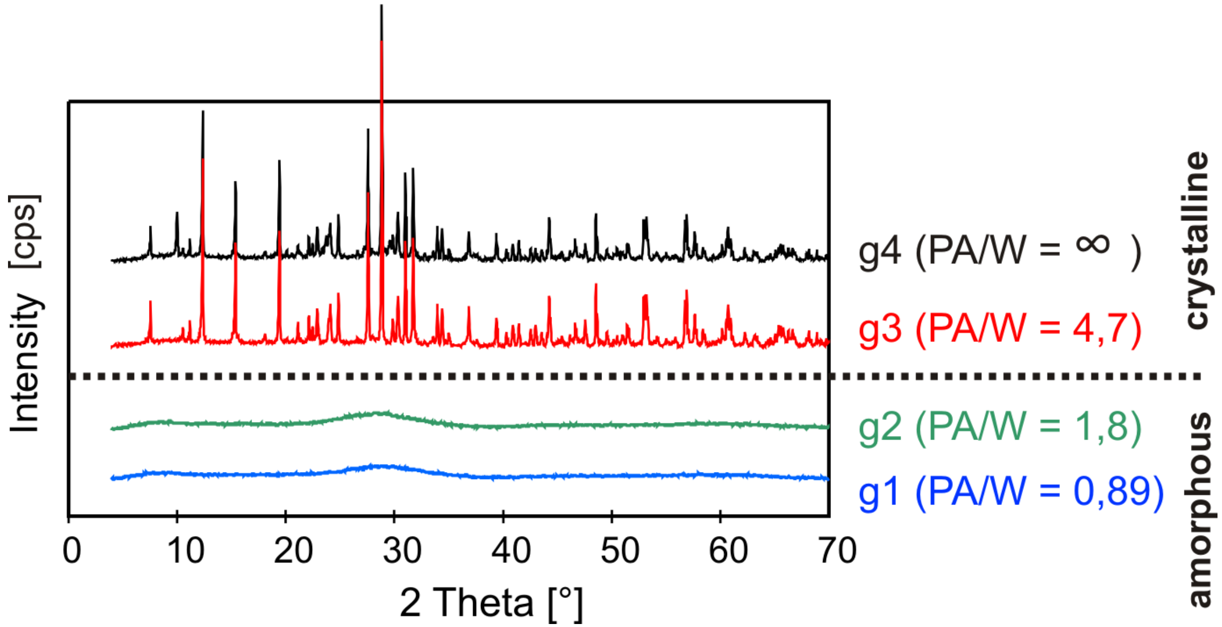
Composition lines with PA/W ratios:

g1: 0.89 g2: 1.8
g3: 4.7 g4: ∞

w.a.: working area with relevant binder action
n.w.: no workability
n.s.: no setting
p.g.: permanent gel-state

Amorphous and crystallized networks with 30 wt.% IO - X-ray diffractograms





high PA content

(cryst. $Fe_3H_9(PO_4)_6{\bullet}6H_2O$)

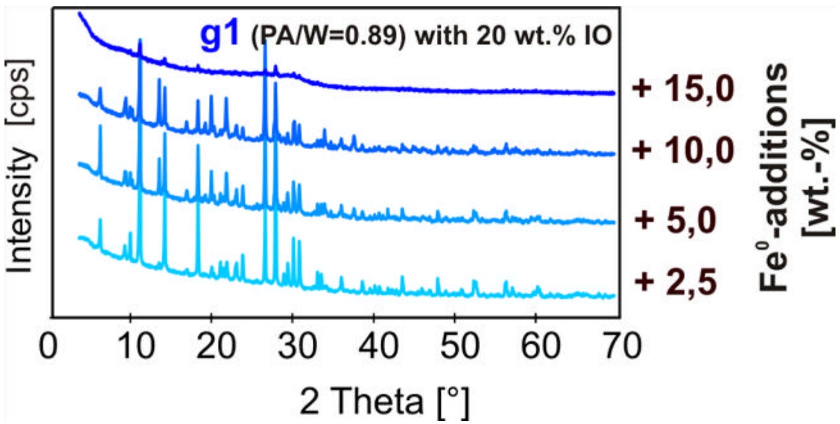
low PA content

(-)

Glass-like materials by sufficient water content

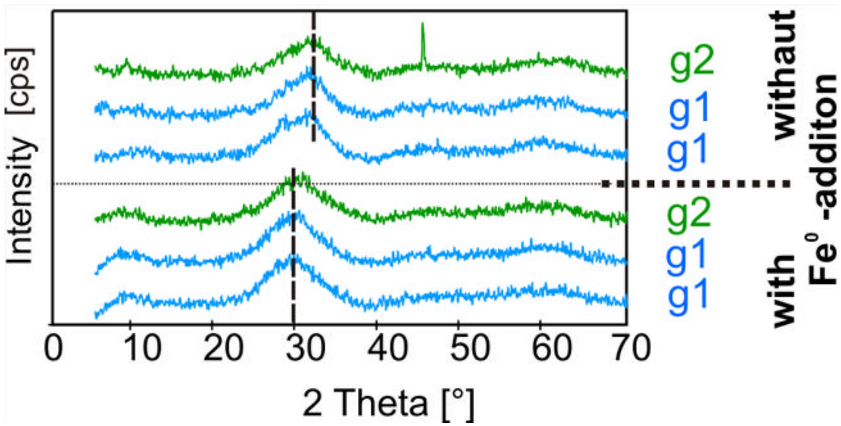
Fe^0 additions in iron-phosphate networks - structural aspects

Sub-stoichiometric addition $Fe^0/Fe^{3+} < 1$



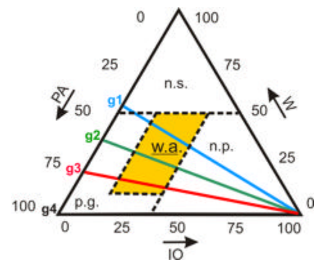
small amounts of Fe^0 (>10 wt.%) → glass-ceramic material

Stoichiometric addition $Fe^0/Fe^{3+} \approx 1$

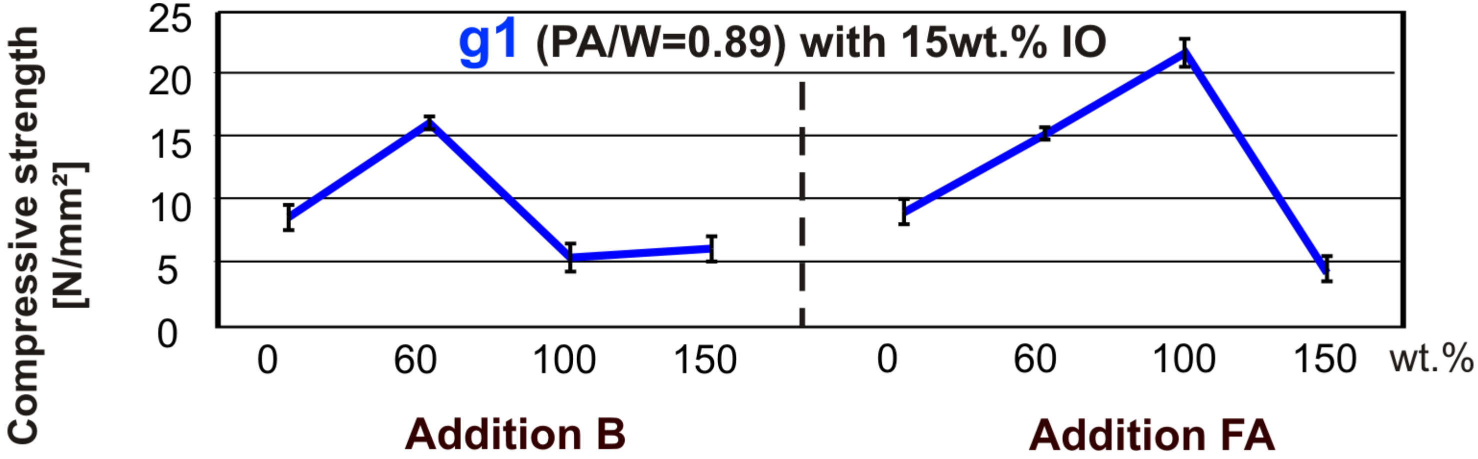


Fe^0 addition → Filling up of the amorphous networks, glass densification

Influence of Basalt (B) and Flyh Ash (FA) of the compressive strength



increase of the chemical durability (attack by boiling water)



composite materials

Enlargement of the strength by a factor of two

5. Summary and Conclusions

Metaclays for geopolymers cements were prepared by a *direct and indirect burning* of a smectitic/illitic clay (Nordhausen, Germany).

- The indirect burning (water vapour) generates *metaclays*, showing already at 750°C *remarkable contents of amorphous aluminosilicates* (XRD, solubility in NaOH).
- In the alkaline solution, the optimum molar Si/Al ratio of 2.2 – 3.0 leads to a *high binder performance* (no contribution of higher values to the strength!)
- The strength of the geopolymers is limited by the formation *of new crystalline phases* (spinel) in the metaclays at higher firing temperatures around 950°C .
- In comparison, the direct burning (air, 850°C) results in not so developed effectiveness and needs more energy, demonstrating the meaning of definite conditions for the thermal activation.

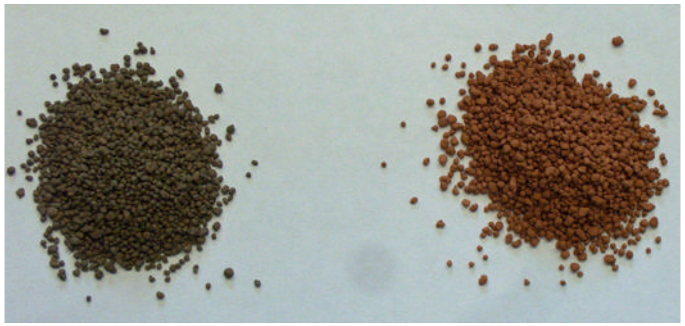
5. Summary and Conclusions

Iron-phosphate binders were generated by acidic activation of an *iron oxyhydroxide by phosphoric acid* (H_3PO_4)

- *Polycondensation* as the dominant reaction is probable in the process of setting (tacky behavior of the binder, XRD).
- *Amorphous networks* are formed in presence of a sufficient amount water and partial *crystallization* can be observed owing to an increasing H_3PO_4 content.
- Small amounts of Fe^0 (iron powder) lead to *glass-ceramic binders* and stoichiometric additions of Fe^0 cause a filling up (*densification) of the amorphous iron phosphate networks* (XRD).
- The addition of *slightly basic mineral powders* (Basalt, Flyh Ash) improves the resistivity against boiling water and the strength of the composite materials.

Both investigations demonstrate the importance of the knowledge of *suitable conditions for the thermal activation of clays* and *for acidic activation of iron oxyhydroxid*, especially the *role of water* in the vapor and in the binder mixtures is exciting.

Thank you for your attention !



Compositions of cements, alkali-activated slags(AAS) and geopolymers