

An approach for the evaluation of local raw material potential for calcined clay as SCM, based on geological and mineralogical data: Examples from German clay deposits

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Abstract. This study gives an overview over the geological and spatial distribution of German clay deposits visualized in a GIS map, which is based on the map of mineral resources, the geological map of Germany and supplemented by active clay pits. The clays are classified regarding their geological context. Representative clays for a certain geological formation are examined closely. Detailed clay mineralogy is determined using XRD. Optimal calcination temperature is defined using TG/DTG. The calcined clays are characterized by XRD and BET. Pozzolanic reactivity is assessed by R³-test and solubility of Al and Si ions in alkaline solution. A correlation between geological origin, chemical-mineralogical composition and pozzolanic reactivity is discussed. The study shows, that a rough estimation of pozzolanic reactivity based on geological data or chemical composition is possible. For a detailed assessment, an elaborate determination of mineralogical phase content or a direct determination of reactivity is necessary.

Keywords: calcined clay, clay deposits, clay mineralogy, pozzolanic reactivity

1 Introduction

One of the most effective attempts to lower the ecological impact of cement production due to CO₂ emissions is the partial substitution of cement clinker. Since established supplementary cementitious materials (SCM) like fly ash and slag stagnate or even decrease in many industrialized countries, the demand for alternative materials will rise in the future [1]. The probably most promising alternative materials are calcined clays. Much research has been done in the past years, focusing primarily on metakaolin [2]. Recently, the focus shifted on calcined natural clays [3,4] which, from an economic point of view, form the most interesting group of new SCM. The pozzolanic reactivity in dependence of the mineralogical clay composition, primarily kaolinite content, has been subject of many studies [5,6], which already allows drawing conclusions on the reactivity based on the mineralogy. In order to enhance the evaluation of clay deposits for the use as SCM, it is important to better understand the influence of mineralogy on reaction behavior and to relate these parameters to the geological setting of the deposit. This could help for a rough assessment of clay deposits based on geological data and maps, which exist for many parts of the world.

In Germany, the current main application fields for clays are the brick, the ceramic and the refractory industry. Lower quantities are used as sealing clays. Kaolin mainly

serves as ceramic raw material, filler for paper, plastics, rubber or colors. In 2015, 5.3 million tons of raw kaolin have been mined leading to 1.1 million tons of kaolin products available for sale. On the other side there were 6.4 million tons of special clay being used for the ceramic and refractory industry plus another 12 million tons of clay used in the brick industry [7].

This study gives an overview over the clay deposits in Germany, including an evaluation of characteristic samples, regarding their applicability as calcined clays as SCM, based on mineralogical characterization and assessment of pozzolanic reactivity.

2 Spatial analysis of clay deposits and selection of clays

On the basis of the maps of mineral resources [8] and Geology of Germany [9] a base map (Fig. 1) was created using *ESRI ArcGIS*. *ArcGIS* is a geographic information system, which allows to collect, analyze and present spatial data. Active clay pits and cement plants were added. Areas with a concentration of clay-deposits were described geologically. From each area, at least one sample was selected for further investigation.

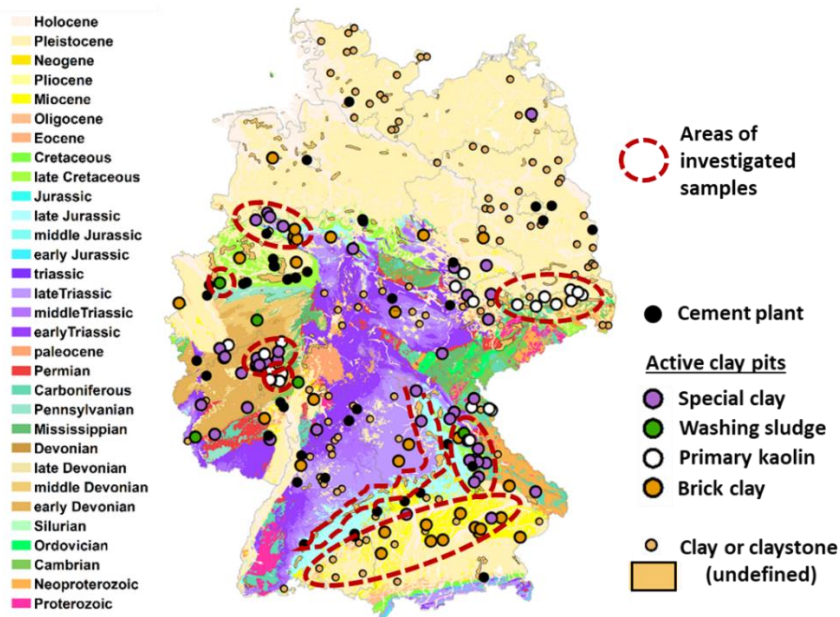


Fig. 1. Geological map of Germany 1:1,000,000 [9] with deposits of clay and claystone [8] and active clay pits

Orange areas and the small orange dots represent clay and claystone, which are not further classified, as they are provided by the map of mineral resources of Germany. The manually added open clay pits are divided in brick clays, special clays, kaolin and washing sludges. Brick clays are clays which are mainly used for the production of

masonry bricks, roof tiles, facing bricks or clinker. Special clays represent the raw material for refractories, acid-resistant and technical ceramics or fine-ceramics. Primary kaolin deposits which are further processed to high-grade products are referred to as kaolin. Washing sludges are residues from processing of other raw materials, for example sand, gravel or also coal. Table 1 gives an overview over the selected clays with reference to their geological origin.

The geographic location of clay deposits plays an important role regarding a use as SCM, since the distance from the pits to potential customers defines a major part of the costs. Beyond that, the geographical location can be referenced with geological maps, as it was done in this study, to get a first idea about the suitability of the clays.

Table 1. Clays selected for investigations and their geological description

Short name	Long name	Geological description
KT	Raw Kaolin Taunus	Primary kaolin deposit accrued by Eocene and Oligocene weathering of Devonian chlorite-rich shale [10]
KUP	Raw Kaolin Upper Palatinate	Primary kaolin deposit formed from Eocene until Miocene by weathering of Carboniferous granite [10]
FUP	Fireclay Upper Palatinate	Sedimentary kaolin-rich clays deposited in the Miocene [11]
RKUP	Recycling Kaolin Upper Palatinate	Secondary component of a Jurassic sandstone, enriched by technical wet-processing [10]
AC	Amaltheen Clay	Early Jurassic marine sediments of a continental shelf [12]
SW	Shale Westerwald	Devonian slate which outcrops in Westerwald clay deposits [13]
SCW	Stoneware Clay Westerwald	Tertiary weathering products of fine-grained Devonian rocks deposited in Eo- until Miocene [12]
CCW	Coal-bearing Clay Westphalia	Secondary component of Upper Carboniferous coal beds [13]
MOSM	Marl Upper Freshwater Mollasse	Upper Eocene to the Upper Miocene sediments resulting from erosion processes of the alps which were deposited in the foreland basin [13]
SLS	Shale Lower Saxony	Cretaceous shale [12]
KS	Kaolin Saxony	Tertiary kaolinisation of a Permian quartz-porphyrity – purified by wet-processing [11]

3 Experimental procedure

The chemical composition of the raw clays was analyzed by means of ICP-OES (*Varian ICP-OES 720 ES*) on solutions of lithium metaborate flux fusions. The clay minerals

where identified by XRD (*PANalytical Empyrean, Bragg-BrentanoHD monochromator, PIXcellID linear detector*) on oriented mounts of the particle fraction smaller than $2\ \mu\text{m}$ following [14]. The samples were measured in air dried and in glycolated condition in order to account for swellable clay minerals. Bulk mineralogy of raw and calcined clays was analyzed on side loaded powder mounts in order to reduce preferred orientation effects. The quantitative phase composition was calculated by Rietveld Refinement using Profex BGMN [15]. For the determination of the amorphous fraction of the calcined samples the external standard method was applied according to [16]. Thermal decomposition of the clays was investigated using TG/DTG (*Netzsch STA 449 F3 Jupiter*) with a heating rate of $2\ \text{K/min}$. The calcination temperature was defined by adding $100\ \text{K}$ to the offset temperature of the main dehydroxylation reaction. The clays were calcinated for 30 minutes in a laboratory muffle furnace using platinum crucibles. The calcined clays were ground in a vibratory disc mill with a speed of $700\ \text{min}^{-1}$ for 10 minutes, using an agate grinding tool. Specific surface area (BET) was measured in a *Horiba S-9601 MP* using nitrogen as absorption gas. The solubility of Al- and Si-ions was determined by elution of the calcined material in NaOH-solution (10 %) [17]. Pozzolanic reactivity was assessed following the R^3 calorimetry test at $40\ ^\circ\text{C}$ [18,19].

4 Results

4.1 Chemical and mineralogical properties of the raw clays

The investigated raw clays are plotted in a ternary diagram (Fig. 2) based on their contents of SiO_2 , Al_2O_3 and $\text{CaO} + \text{MgO}$, normalized to the sum of these components. The relevant silica-rich region of the diagram is enlarged.

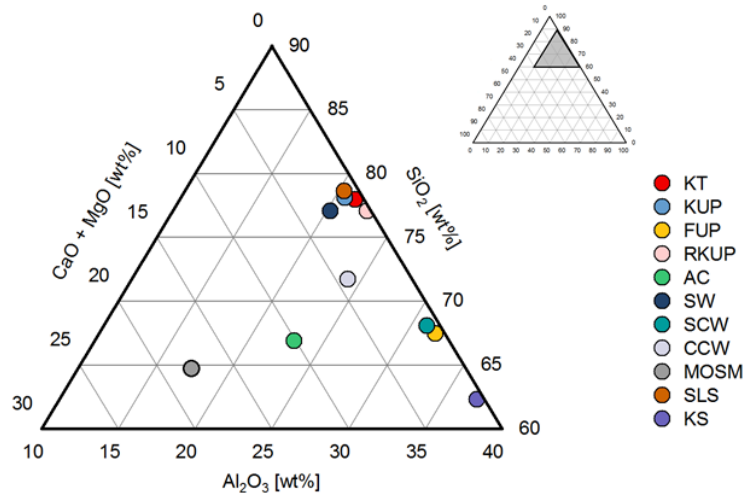


Fig. 2. Plot of the investigated raw clays in the ternary diagram based on the contents of Al_2O_3 , SiO_2 and $\text{CaO} + \text{MgO}$ normalized to the sum of them

The three clays in the alumina-rich right corner are sedimentary kaolinitic clays and technically processed primary kaolin (FUP, SCW, KS). The marl (MOSM) and the calcite-bearing Amalthean clay (AC) can be differentiated by their CaO + MgO content. The low grade kaolinitic clays plot in the silica-rich half of the SiO₂-Al₂O₃-axis and cannot be differentiated in this way. Ternary diagrams based on the chemical composition can help to separate the kaolinite-rich clays from the low kaolinite clays (if there is no other major Al₂O₃ source) or marls from lime-free clays but are unsuitable to differentiate between different low grade kaolinitic clays with several other clay minerals. Nevertheless, chemical compositions are often provided by clay-suppliers and can be used for a first rough classification. The mineralogical composition of the different clays in Table 2 and is discussed together with the reactivity below point 4.3.

Table 2. Mineralogical composition of the analyzed clays: Qtz=Quartz, K_{md}=moderately disordered kaolinite, K_{hd}=highly disordered kaolinite, Ill=illite, I-S=illite-smectite, Sm=smectite, Ms=muscovite, Chl=chlorite, Cc=calcite, Dol=dolomite, Fsp=feldspar, Rt=rutile, An=anatase, Py=pyrite, He=hematite, Goe=goethite, Sid=siderite, Am=amorphous

	FUP	SW	CCW	KT	AC	MOSM	RKUP	KUP	SLS	SCW	KS
Qtz	12	21	16	38	20	18	48	33	37	18	16
K _{md}	-	7	-	20	-	8	17	26	7	-	25
K _{hd}	74	-	10	-	23	-	28	-	-	40	59
Ill	3	-	11	-	-	-	-	-	-	-	-
I-S	8	-	24	-	32	-	-	-	40	20	-
Sm	-	-	-	-	-	25	-	-	-	-	-
Ms	-	51	-	36	5	19	3	36	15	18	-
Chl	-	19	1	-	6	5	-	-	-	-	-
Cc	-	-	< 1	-	7	7	-	-	-	-	-
Dol	-	-	1	-	1	10	-	-	-	-	-
Fsp	-	-	-	-	4	7	-	-	-	-	-
Rt	1	1	-	1	< 1	1	-	1	-	2	-
An	1	-	0	-	2	-	< 1	-	1	-	1
Py	-	-	-	-	1	-	-	-	-	-	-
He	-	-	< 1	-	-	-	< 1	-	-	2	-
Goe	-	-	-	5	-	-	3	4	-	1	-
Sid	-	-	1	-	-	-	-	-	-	-	-
Am	-	-	35	-	-	-	-	-	-	-	-

4.2 Characterization of calcined clays

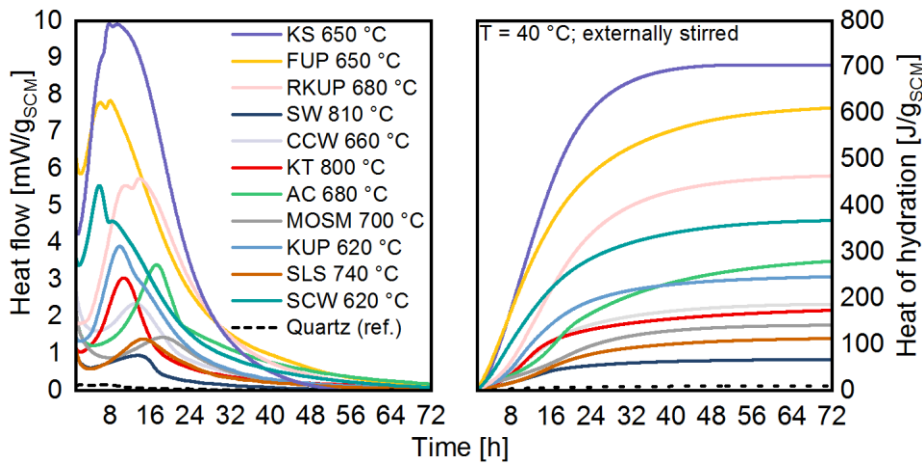
Table 3 shows the X-ray-amorphous content after calcination, the specific surface area after grinding and the calcination temperatures that were defined based on the end set temperatures of the main dehydroxylation reaction in the DTG data.

Table 3. Calcination temperatures, amorphous content and BET after calcination and grinding

	FUP	SW	CCW	KT	AC	MOSM	RKUP	KUP	SLS	SCW	KS
T _{calc} [°C]	650	810	660	800	680	700	680	620	740	620	650
Am. [wt%]	76	37	49	19	43	31	33	23	36	56	81
BET [m ² /g]	44.1	9.1	40.2	10.0	30.2	17.3	8.4	8.7	16.5	32.2	n.d.

4.3 Reactivity

The heat release of the different calcined clays during the R³ calorimetry test is shown in Fig. 3. The first 1.2 h are cut off, according to Li et al. [19]. Quartz powder was used as an inert reference. The investigated materials show a broad variation, regarding the quantitative heat release as well as the reaction kinetics. The high grade kaolinitic clays cause two maxima which are differently pronounced, referring to the silicate and aluminate reaction. The sedimentary kaolinitic clays (FUP & SCW) provide a fast reaction with a first heat flow maximum below 8 h, which probably results from a faster release of especially Al ions due to the high amount of disordered kaolinite and a high specific surface area. The primary kaolins (KS, KT & KUP) and the recycling kaolin (RKUP), which show a higher degree of order and therefore also a lower surface area provide a slower reaction and the two maxima merge to one. The clays with lower amount of kaolinite react clearly slower with one broad reaction maximum, which is due to the lower release of Al ions.

**Fig. 3.** Development of the heat release normalized per gram of calcined clay during R³ calorimetry test (left) and cumulative heat (right) from 1.2 to 72 hours

The correlation between Al₂O₃ content and reactivity (Fig. 4) is good for high kaolinite contents, where other clay minerals do not play an important role. Clays with lower kaolinite content do not differ significantly in Al₂O₃ content which is why this

parameter cannot be used to assess them. As has been shown before [5,6], the decisive criteria for reactivity is the overall kaolinite content of the raw clay. If it exceeds about 40 wt%, the contribution of other components to the heat flow is nearly negligible. In the area of lower kaolinite contents, the role of the other clay minerals gains significance. This is shown by the clays with a kaolinite content below 30 wt%. Here, clays containing significant amounts of illite, smectite or illite-smectite mixed layer minerals provide a clearly higher heat development during the R³ calorimetry test than those containing mainly mica and quartz. This is in good consistency with investigations on reactivity of single phyllosilicates [20].

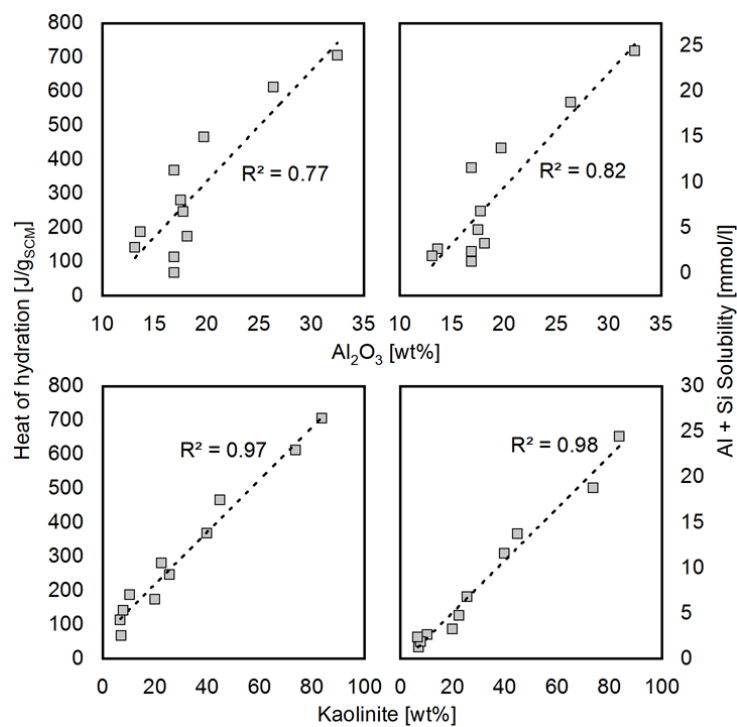


Fig. 4. Influence of Al₂O₃ (top) and kaolinite (bottom) content on heat of hydration during R³ calorimetry test (left) and on solubility of Si and Al ions (right)

5 Conclusion

Geological data can allow conclusions on the type of clay deposits and therefore help for a rough estimation of suitability. In order to derive a more precise assessment, a comprehensive mineralogical analysis is requisite. Particularly for low-grade kaolinitic clays, the impact of other clay minerals is significant. An evaluation based on the chemical composition does not work for low-grade kaolinitic clays, since the difference in

Al_2O_3 content is not significant. For the assessment of pozzolanic reactivity, the R^3 calorimetry test and the solubility of Al and Si ions show very good consistency.

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