

SUMMARY OF CLAY-MINERAL STUDIES IN GERMANY, 1954 AND 1955

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ABSTRACT

Correns and Lippmann have extended the work carried out in England on swelling chlorites by some investigations on Keuper clays.

Dietzel has succeeded in showing that the infrared absorption band of kaolinite at 2.7μ has two peaks which can be correlated with two different kinds of (OH) groups in the structure.

The "fire-clay" type of clay mineral has been found in Grossalmeroder clay by Lippmann and in Frantex clay from Provins by von Engelhardt. In Frantex clay especially the layer sequence is highly disordered. Halloysite is distinguished from these minerals by its greater layer spacing and metahalloysite by its tubular morphology.

Winkler has studied the particle size distribution of numerous brick clays and has established that the mineral must have a certain proportion of fine and coarse clay and fine sand, but also a very smooth particle size distribution curve from the finest to the coarsest particles if the clay is to be suitable for thin-walled ware.

The clay mineral section of the Deutsche Keramische Gesellschaft tested various methods for quantitative clay mineral analysis. More than 20 laboratories used the following methods: x-ray analysis, dilatometer analysis, D.T.A., dehydration curves, microscopic analysis, and the determination of free silica by solution in phosphoric acid.

By the investigation of mixtures made up of the purest quartz, feldspar, halloysite, illite, kaolinite, montmorillonite and "fire-clay" mineral, the correct values were found for the most part within a few percent.

In the investigation of natural clays, greater differences were found, amounting to as much as 10 percent. Von Engelhardt especially investigated the errors arising with Geiger counter x-ray equipment.

Lippmann (1954) found in a red Keuper clay from Zaiserweiher a mineral of the swelling chlorite type, which Honeyborne (1951) had first noted, and the x-ray patterns of which were explained by Stephen and MacEwan (1951). The Zaiserweiher mineral also shows a basal reflection at $d = 28 \text{ \AA}$, which corresponds to a thickness of two unit layers of the chlorite structure. This reflection is shifted, by treatment of the clay with glycerin, to a value of 32 to 33 \AA . In patterns from water-moistened preparations the reflection lies at about 30 \AA . Lippmann proposed to call this mineral "corrensite."

Lippmann (1953) found in clay from Grossalmerode a mineral that corresponded in its x-ray diffraction pattern to the fire-clay type described by Brindley and Robinson (1946). In Provins, France, von Engelhardt (1954) found a similar mineral in the Frantex clay, which is used as a filler for rubber. He noted, however, still greater disorder in the sequence of layers. The fire-clay mineral meanwhile was found in a number of clays, e. g., J. L. of Provins, HSH1 of Hettenleidelheim, Schwarzenfeld, and others. The disorder of the sequence of layers is occasionally somewhat greater or smaller. It is of interest that in a well-ordered coarsely crystalline kaolinite, as for example the kaolin of Schnaitenbach OF, a similar lattice disorder can be produced by suitable grinding and

that analogous lattice disorder in graphite has been known for many years (Hofmann and Wilm, 1936, 1944; Jagodzinski, 1949; Franklin, 1951).

In Italy it is useful for ceiling construction to make use of especially thin-walled ceiling-tiles. Winkler (1954) showed that the requirement for this is a raw clay having appropriate amounts of fine and coarse clay and fine sand, but also a very smooth particle-size distribution curve from fine clay to coarse sand. When such clays are not present in nature, they can be manufactured in adequate quality by mixing different clays.

Scholze and Dietzel (1955) succeeded in showing that the infrared absorption band of kaolinite at 2.7 microns has two peaks. According to position and intensity, they believe that the peak at 2.71 microns can be correlated with the outer OH groups lying at the surface of the octahedral layers, and the peak at 2.76 microns with the inner OH groups lying between Al and Si layers.

It is well known (Hofmann, Endell, and Wilm, 1934) that some bentonites, especially those of southeastern Europe, contain considerable amounts of free silicic acid, the x-ray reflections of which correspond with those of opal. In electron micrographs this silicic acid shows as very fine grains. The x-ray pattern of this opal-like silicic acid was formerly explained by assuming that the reflections of high cristobalite are present, as well as a small amount of low cristobalite. O. W. Flörke (1955) now shows that here we have no high cristobalite, but a one-dimensionally disordered low cristobalite. The Si-O-tetrahedral layers forming the cristobalite lattice are arranged on one another in an irregular sequence.

Von Engelhardt (1955) thoroughly studied the possibilities of the quantitative phase analysis of clays with x-rays using the x-ray counter spectrometer. If texture and absorption in the individual crystal are avoided (equivalent grain size below 6 microns); if the size of the preparation is correct and if the x-ray absorption coefficient of the various minerals is taken into account; then the absolute intensity of the reflections for quartz, kaolinite, and illite depends on the grain size and on the occurrence. Von Engelhardt believes that this is possibly due in part to the presence of x-ray-amorphous substance on the surfaces of the crystals (See also studies on quartz by Nagelschmidt, Gordon, and Griffin, 1952; 1955.). With montmorillonite additional attention, of course, must be paid to the influence of the layer distance on the x-ray intensities. After

TABLE I. — QUANTITATIVE ANALYSES OF MIXTURE, COMPOSITION I: QUARTZ, 47 PERCENT; HALLOYSITE, 38 PERCENT; ILLITE, 15 PERCENT (CLAY MINERAL COMMITTEE, 1955)

Lab. no.	Series of tests Method	Mineral analysis (percent)		
		Quartz	Halloysite	Illite
5	x-ray (film)	50	35	15
4	x-ray (Geiger counter)	47	34	19
7	Dil.	40-45	40-45	15-20
11	D.T.A.	55	30	15
12	D.T.A.	47	31	22
13	D.T.A.	40	40	20
18	micro.	48	35	17
20	H ₃ PO ₄	48 ¹		

¹ Free SiO₂

TABLE 2. — QUANTITATIVE ANALYSES OF MIXTURE, COMPOSITION III: QUARTZ, 6 PERCENT; FIRE CLAY, 47 PERCENT; MONTMORILLONITE, 47 PERCENT (CLAY MINERAL COMMITTEE, 1955)

Lab. no.	Series of tests Method	Mineral analysis (percent)			
		Quartz	Fire clay	Montmorillonite	Other
1	x-ray (film)	3	53	44	
2	x-ray (Geiger counter)	6	47	47	
3	x-ray (Geiger counter)	8	47	45	
7	Dil.	5-10	35-40	55-60	
11	D.T.A.	5-10	45	45	
12	D.T.A.	10	40	45	5 (halloysite)
13	D.T.A.	3	48	42	7 (feldspar)
17	Dehydration	8	45	47	
20	H ₃ PO ₄	6 ¹			

¹ Free SiO₂

consideration of all these influences in mixtures of known minerals errors of analysis can be reduced to a few percent.

The Clay Mineral Committee of the Deutsche Keramische Gesellschaft started several years ago, in cooperation with the Deutsche Mineralogische Gesellschaft, a comparative test of the various methods of quantitative clay-mineral analysis. More than 20 industrial and university laboratories used the following methods: x-ray analysis with film and Geiger-counter equipment, differential thermal analysis (D.T.A.), dilatometer analysis (Dil), dehydration curves, microscopic analysis, and determination of free silicic acid by solution in H₃PO₄, and in some cases, rational analysis. To improve the control, complete chemical analyses were always carried out by several laboratories.

Mixtures for analysis were prepared from components that, so far as possible, were monomineralic (kaolinite, fire-clay mineral, halloysite, illite, montmoril-

TABLE 3. — QUANTITATIVE ANALYSES OF MIXTURE, COMPOSITION IV: QUARTZ, 5 PERCENT; FELDSPAR, 8 PERCENT; MONTMORILLONITE, 11 PERCENT; KAOLINITE, 76 PERCENT (CLAY MINERAL COMMITTEE, 1955)

Lab. no.	Series of tests Method	Mineral analysis (percent)			
		Quartz	Feldspar	Montmorillonite	Kaolinite
1	x-ray (film)	5	5	12	78
3	x-ray (Geiger counter)	5	10	10	75
4	x-ray (Geiger counter)	7	7	6	80
7	Dil.	5	5	10	80
11	D.T.A.	5-10	—	—	80
13	D.T.A.	6	24	5	65
17	Dehydration	5-10 (ca. 8)	10	10-15 (ca. 12)	70
18	Micro.	7	8	7	78
20	H ₃ PO ₄	5 ¹			

¹ Free SiO₂

TABLE 4. — MINERAL ANALYSES OF BENTONITE¹ FROM NIEDERBAYERN (CLAY MINERAL COMMITTEE, 1955)

Series of tests		Mineral analysis (percent)				
Lab. no.	Method	Montmorillonite	Mica	Kaolinite	Quartz	Others
1	x-ray (film)	50	some	40	5	
2	x-ray, D.T.A.	40	10-15	40	5	
18	x-ray, micro.	>35	10-15	<45	5	5
20	H ₃ PO ₄	—	—	—	4	
23	Dil.	40-60	—	20-30	15-30	

¹ Chemical analysis: SiO₂, 52.1 percent; Al₂O₃, 28.3 percent; Fe₂O₃, 5.0 percent; MgO, 2.3 percent; K₂O, 1.2 percent; loss on ignition, 9.9 percent.

TABLE 5. — MINERAL ANALYSES OF CLAY¹ (OBERWINTER BLAUTON) (CLAY MINERAL COMMITTEE, 1955)

Series of tests		Mineral analysis (percent)			
Lab. no.	Method	Kaolinite	Sericite	Quartz	Other
1	x-ray (film)	30	35	35	
2	x-ray, D.T.A.	30	40-45	25-30	
18	x-ray, micro.	24	34	40	4 (incl. feldspar)
20	H ₃ PO ₄	—	—	30-31	
23	Dil.	ca. 20	40-50	30-40	

¹ Chemical analysis: SiO₂, 61.6 percent; Al₂O₃, 24.8 percent; K₂O, 4.15 percent; loss on ignition, 5.9 percent.

TABLE 6. — MINERAL ANALYSES OF ELUTRIATED SCHLETTAER SOIL¹ (DR. MIELDS) (CLAY MINERAL COMMITTEE, 1955)

Series of tests		Mineral analysis (percent)			
Lab. no.	Method	Mica (Illite)	Kaolinite	Quartz	Others
1	x-ray (film)	45	35	20	
2	x-ray, D.T.A.	20	30	25-30	20 (montmorillonite)
18	x-ray, micro.	38	23	30	9 (incl. feldspar)
20	H ₃ PO ₄	—	—	22-23	—

¹ Chemical analysis: SiO₂, 63.6 percent; Al₂O₃, 21.8 percent; MgO, 2.6 percent; K₂O, 4.6 percent; loss on ignition, 5.7 percent.

lonite, quartz, feldspar). The compositions of these mixtures were not known to the analysts. They were also given the pure components in order to calibrate their methods. Quartz and feldspar contained considerable amounts coarser than 5 microns. This corresponds with the natural occurrence, but renders the x-ray analysis, for example, more difficult.

It seemed that in the best results the correct values were attained independently of the methods employed, within a few percent. The determination of free silica by solution in H₃PO₄ proved to be especially reliable. The tables of mixtures I, III and IV (Tables 1, 2, 3) give only examples of the many mixtures investigated and contain only the best results.

Later a large number of natural clays were examined, which contained several minerals. Complete chemical analysis of these clays provided a check on the other methods. In the last test series of that kind, especially experienced laboratories reached comparatively satisfactory results with various methods. The differences, however, amounted to as much as 10 percent. X-ray diffraction (including film and Geiger-counter equipment) is perhaps the best individual method. The most practical procedure is undoubtedly the combination of several methods, and, if time permits, fractionation into several grain sizes. Tables 4, 5, and 6 give a few examples. The full tables of these analyses are available on request.

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