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Research paper

Comparison of methods for distinguishing sodium carbonate activated from natural sodium bentonites

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ABSTRACT

A lot of natural Ca/Mg-bentonites are turned into Na-bentonites. By adding sodium carbonate to a Ca/Mg-bentonite in the presence of some water Na^+ enters the interlayer and Ca/Mg-carbonates precipitate outside. Natural Na-bentonites and activated Na-bentonites are rather similar. Therefore, in the present study methods are tested to distinguish both. This is relevant not only for customs but also for research and development. For activation different amounts of sodium carbonate are added. The dosage ranges from a few % of the CEC to slightly above the CEC corresponding to 1–5 mass% Na_2CO_3. Also the water content may vary from the dried state at which the actual activation (cation exchange) does not take place up to the presence of excess water leading to a complete reaction. Altogether four cases had to be considered separately (Na_2CO_3 above CEC + excess water or dry and Na_2CO_3 much below the CEC + excess water or dry). If water was absent (cation exchange was not complete) the sodium carbonate phases could be detected by XRD, IR, or with STA–MS measurements. This result was expected but surprisingly, STA–MS–CO_2 measurements were found to be applicable even in the most difficult case (sodium carbonate addition below CEC and excess of water = reaction complete). In the case of some samples activated with 2 mass% sodium carbonate only, a weak STA–MS–CO_2-peak was observed at about 100 °C. Unprocessed materials are free of any carbonates which decompose around 100 °C. Therefore, this 100 °C peak indicates alkaline activation. This method was applied to five real products with unknown activation and two of which were found to be activated. The pH of the activated materials was only slightly higher than that of a natural Na-bentonite. The measured difference of 0.3 pH units is not considered to be sufficient to unambiguously conclude alkaline activation.

1. Introduction

A large amount of bentonite is used because of its rheological properties such as thixotropy. Examples are bentonite drilling mud and paint additive. The rheological properties along with others (such as water uptake; Kaufhold et al., 2010) strongly depend on the type of interlayer cation balancing the permanent charge of the smectites. The common exchangeable cations are Ca^{2+} and Mg^{2+}. However, a few bentonites (smectites) are dominated by exchangeable Na^+ as e.g. the famous Wyoming bentonites (Grim and Güven, 1978). To improve the rheological properties of Ca/Mg-bentonites, Hofmann and Endell (1936) suggested the use of sodium carbonate for the exchange of interlayer Ca^{2+} or Mg^{2+} by Na^+. Large amounts of NaCl would be necessary because Ca^{2+} and Mg^{2+} are selectively adsorbed in contrast to Na^+ (e.g. Lagaly, 1993; McBride, 1979). The presence of the carbonate or hydrogencarbonate anion, however, leads to the formation of rather insoluble Ca/Mg-carbonates (Lagaly et al., 1981). Precipitation of these carbonates occurs outside the interlayer. Therefore, Ca^{2+} and Mg^{2+} have to leave the interlayer which in turn indirectly promotes the cation exchange.

The optimum amount of sodium carbonate to be added to a Ca/Mg-bentonite is commonly determined empirically by investigation of the rheology of a set of different bentonites with different ratios of sodium carbonate and bentonite. Theoretically, the optimum amount should correspond to the CEC and further addition should not change the bentonite properties anymore. However, adding slightly more sodium carbonate than the CEC often yields better results (e.g. rheology), which is probably related to pH effects (Alther, 1986). Assuming a bentonite with a CEC of 90 meq/100 g, considering the molar mass of sodium carbonate accounting for almost 106 g/mol, and considering the two charges of both Na^+ cations of the sodium carbonate leads to 4.8 mass% sodium carbonate at which the CEC is reached. However, the CEC of most bentonites is lower. In the case of 70 meq/100 g CEC of a bentonite 3.7 mass% sodium carbonate would be sufficient to saturate all charges.

Technically activated bentonites are produced at production lines all over the world, packed, and shipped to their destination. For

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international shipping different documents are required including a customs declaration (technically produced or natural materials are commonly distinguished). For the customs, controlling custom regulations is impossible without a suitable method. Distinguishing both types of materials is also relevant in research and development: When comparing different products, it is essential to know whether and how a bentonite was activated or not. Activation is often carried out together with strong shearing (e.g. in extruders) which in turn results in improved bentonite properties (induced by shearing). Any scientific work carried out on bentonite, therefore, should be based on material with known history.

Different analytical tools were suggested to unambiguously distinguish natural Na-bentonites from alkaline activated materials. Fahn (1964) suggested to consider alkalinity, pH of the dispersion, CO_2 and Na_2O_3 content, and water soluble salts to detect activation. However, the pH value of natural Na-bentonites can exceed 10 (Kaufhold et al., 2008) and bentonites from some deposits are known to contain natural soluble salts. Although time consuming the method proposed by Fahn (1964) is supposed to work for most bentonites but could fail in the case of natural Na-bentonites with soluble salts (e.g. Morocco). Steudel et al. (2013) proposed using thermal analysis for the detection of technically activated Na-bentonite. However, Steudel et al. (2013) only used one type of sodium carbonate containing the characteristic impurities such as thermonatrite and trona. Hence, in order to assess the proposed methods in the present study different sodium carbonate samples and a set of well characterized bentonites were used. The technical activation process is commonly run with 30–40 mass% water which may not be sufficient for completing the activation. Hence some undissolved and unreacted sodium carbonate may still be present. Therefore, in order to be representative of real systems, the water content before and after addition of the sodium carbonate was varied.

The aim of the present study is to compare different methods with respect to the possibility to unambiguously distinguish technically activated Na-bentonites from natural ones.

2. Materials and methods

The materials used are listed in Table 1.

Alkaline bentonite activation is based on the reaction of a Ca/Mg-bentonite with Na_2CO_3 which can be applied as different phases/products. For the activation technical Na_2CO_3 rather than p.a. or food grade is required. The technical product may vary with respect to the contents of different phases, water content, and other chemical impurities. Anhydrous sodium carbonate is relatively rare because it tends to react with water to at least form the mono-hydrate (thermonatrite). The following phases may occur in technical sodium carbonate (TSC):

1) Na_2CO_3 = natrite (anhydrous sodium carbonate)
2) $Na_2CO_3 * H_2O$ = thermonatrite (sodium carbonate monohydrate)
3) $Na_2CO_3 * 7H_2O$ = <no mineral name> (sodium carbonate heptahydrate)
4) $Na_2CO_3 * 10H_2O$ = natron (sodium carbonate decahydrate)
5) $Na_3(CO_3)(HCO_3) * 2H_2O$ = trona (sodium carbonate hydrogen carbonate)
6) $NaHCO_3$ = nahcolite (sodium hydrogen carbonate).

Because of the variety of phases which may occur in TSC products, different types of sodium carbonate were used (samples beginning with #S). Samples beginning with #P are actual industrial products with limited information about a possible alkaline activation. #BN samples are natural Na-rich bentonites which were not in contact with any sodium carbonate. The #LA samples represent Ca/Mg-bentonites (bentonites in which the interlayer is dominated by Ca^{2+} and/or Mg^{2+}). #LA samples were treated differently in laboratory. The #LA-0 samples are the untreated precursor materials of those samples which were modified by sodium carbonate. Both the amount of sodium carbonate and the type of addition/activation were varied. For technical activation different water contents are used. The actual activation, however, does not take place in the absence of water. The actual activation which is the cation exchange of dry activated materials takes place if water is added, e.g.

Table 1
Materials used for the present study.

Sample ID	Material	Information	Reference
S1	Na_2CO_3	Technical Na_2CO_3 provided by S&B, Landshut	S&B, Landshut
S2	Na_2CO_3	Merck	Merck
S3	Na_2CO_3 Merck	$NaHCO_3$	Merck
S4	Na_2CO_3	Trona (mineral piece)	Owens Lake, CA, US
P1	Industrial bentonite product	Catsan clumbing	Mars Inc.
P2	Real bentonite product	Catsan Ultra	Mars Inc.
P3	Real bentonite product	Technically activated with 3% S1	S&B, Landshut
P4	Real bentonite product	Unknown activation	S&B, Marl
P5	Real bentonite product	Waldo North (MK11)	Klinkenberg (2008)
BN1	Natural Na bentonite	Sample B8 (Wyoming)	BGR projects (details below)
BN2	Natural Na bentonite	Sample B11 (India)	BGR projects (details below)
BN3	Natural Na bentonite	Sample B24 (Morocco)	BGR projects (details below)
LA6-0	Bentonite before activation	Sample B6 (Milos), natural state	BGR projects (details below)
LA6-2A	Bentonite. Lab activated	B6 with S2 (2 mass%, added in dry state)	Produced in laboratory
LA6-2D	Bentonite. Lab activated	B6 with S2 (2 mass%, dispersed and dried)	Produced in laboratory
LA6-5A	Bentonite. Lab activated	B6 with S2 (5 mass%, added in dry state)	Produced in laboratory
LA6-5D	Bentonite. Lab activated	B6 with S2 (5 mass%, dispersed and dried)	Produced in laboratory
LA16-0	Bentonite before activation	Sample B16 (Bavaria), natural state	BGR projects (details below)
LA16-2A	Bentonite. Lab activated	B16 with S2 (2 mass%, added in dry state)	Produced in laboratory
LA16-2D	Bentonite. Lab activated	B16 with S2 (2 mass%, dispersed and dried)	Produced in laboratory
LA16-5A	Bentonite. Lab activated	B16 with S2 (5 mass%, added in dry state)	Produced in laboratory
LA16-5D	Bentonite. Lab activated	B16 with S2 (5 mass%, dispersed and dried)	Produced in laboratory
LA19-0	Bentonite before activation sample	B19 (Almeria), natural state	BGR projects (details below)
LA19-2A	Bentonite. Lab activated	B19 with S2 (2 mass%, added in dry state)	Produced in laboratory
LA19-2D	Bentonite. Lab activated	B19 with S2 (2 mass%, dispersed and dried)	Produced in laboratory
LA19-5A	Bentonite. Lab activated	B19 with S2 (5 mass%, added in dry state)	Produced in laboratory
LA19-5D	Bentonite. Lab activated	B19 with S2 (5 mass%, dispersed and dried)	Produced in laboratory

More information about bentonites B6, B8, B11, B16, B19, and B24 is provided by:
BGR project publications: Kaufhold and Dohrmann (2008), Kaufhold and Dohrmann (2009), Kaufhold and Dohrmann (2010a), Kaufhold and Dohrmann (2010b), Kaufhold et al. (2010), Ufer et al. (2008).