

Additional Experimental Data

Impact of bentonite on flocculation using Omysed

I. Materials

I.1. Sediment sample

The sediment sample “*Wasserhaltung 6, Becken 2*” has been provided on 19 March 2015 from RWE Power AG.

The total solid (TS) content, pH, conductivity and charge is measured (Table 1).

The provided sample has a TS content of 27.9% after homogenization with mechanical stirring. The sample is diluted down to 2.5% solid content for evaluating the flocculation performance. The provided sample is brown, nearly black, of very fine and oily consistency (Figure 1).

Table 1: Characterization of the sludge sample “*Wasserhaltung 6, Becken 2*” sample from RWE Power AG (Germany).

Sample	Wasserhaltung 6, Becken 2
Lab name	20150320-WH6-Be2-500mm
Initial TS (%)	24.2
pH	7.1
Conductivity (mS/cm)	225
Charge (mVal/g)	22.3 (anionic)



Figure 1: Sample “*Wasserhaltung 6, Becken 2*” from RWE Power AG (Germany)

I.2. Phyllosilicate samples

Four bentonite samples are provided. The mineralogical composition of these samples is investigated by XRD (Table 2).

Three samples (Bentonite C2, Bentonil XR and Tixoton) show clay concentration of “Montmorillonite / Beidellite” between 66 and 84%. The Terrana sample shows a clay concentration of “Montmorillonite / Beidellite” of 12%.

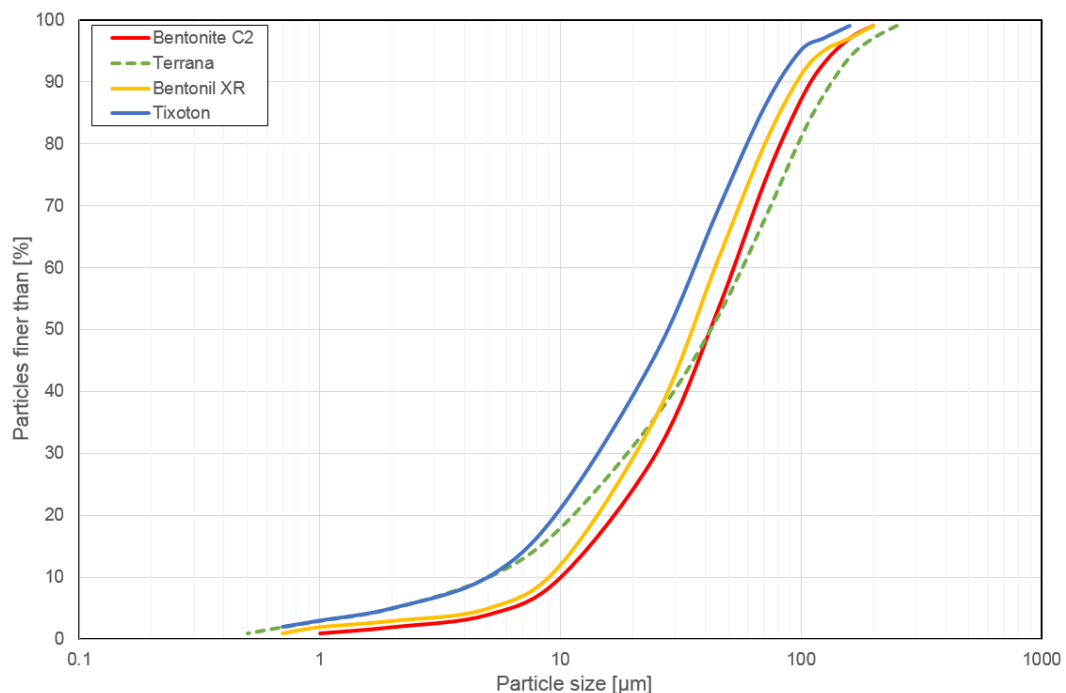
Table 2: Mineralogical characterization of the phyllosilicates used for the flocculation tests.

N°	Samples name	Mineral type	Main Mineral composition (%)		
			Montmorillonite Beidellite	Vermiculite	Quartz
1	Bentonite C2	Na-bentonite	70	0	16
2	Terrana	Clay	12	39	14
3	Bentonil XR	Na-bentonite	84	0	5
4	Tixoton	Na-bentonite	66	0	15

The granulometry of the dry samples is also analysed using a Malvern 3000 (Table 3) and shows the same range of particle size distribution with d_{50} between 28 - 42 mm and a top cut (d_{98}) between 132 – 211 mm.

Table 3: Granulometry of the samples used during the flocculation trials.

N°	Samples name	Mineral type	Granulometry (mm)	
			Median (d_{50})	Top Cut (d_{98})
1	Bentonite C2	Na-bentonite	42.3	177
2	Terrana	Clay	41.7	211
3	Bentonil XR	Na-bentonite	35.4	163
4	Tixoton	Na-bentonite	27.9	132



Graph 1: Particle size distribution of the phyllosilicates used during the flocculation trials

The charge of the phyllosilicates is measured by titration using a particle charge detector (PCD). The three samples Bentonite C2, Bentonil XR and Tixoton, show a higher anionic charge between 1030 – 1317 mVal/g, while the Terrana sample shows only a low anionic charge of 227 mVal/g (Table 4)

Table 4: Charge of the phyllosilicates used during the flocculation trials.

N°	Samples name	Charge (mVal/g)
1	Bentonite C2	1317 ± 67 (anionic)
2	Terrana	227 ± 15 (anionic)
3	Bentonil XR	1147 ± 82 (anionic)
4	Tixoton	1030 ± 56 (anionic)

I.3. Surface-treated calcium carbonate (Omyased)

Omyased, a surface-treated calcium carbonate comprising a coating is prepared and diluted down to 10% TS with deionized water for the flocculation lab testing. The particle size distribution is measured on site using the standard Sedigraph method (Table 5).

Table 5: Particle size distribution of Omyased.

	Sedigraph standard					
	<1 mm (%)	<2 mm (%)	<5 mm (%)	d ₅₀ (mm)	d ₉₈ (mm)	SAA (m ² /g)
Omyased	43.3	79.5	97.9	1.15	5.24	37.3

The calcium carbonate used for the preparation of the surface-treated calcium carbonate is a surface-modified calcium carbonate (MCC) and the cationic coating is provided by the dosage of Catiofast BP at 1.8%, based on the calcium carbonate weight. The repartition of the cationic charge within the surface of the calcium carbonate or within the aqueous phase of the Omyased slurry is investigated (Table 6). The charge distribution on the calcium carbonate surface is calculated accordingly (Table 7).

Table 6: Cationic charge distribution between the surface of the calcium carbonate and the aqueous phase of the slurry for Omyased.

	Cationic charge (mVal/g)	Charge distribution
Total slurry	173.5	100%
Aqueous phase	67.4	38.8%
calcium carbonate surface	106.1	61.2%

Table 7: Cationic charge distribution on the surface of the calcium carbonate.

	Catiofast BP
Dosed, based on calcium carbonate weight	1.8%
Estimated on the calcium carbonate surface, based on the charge distribution	1.1%
Distribution on the calcium carbonate surface (mg/m ²)	0.3

II. Sample preparation and flocculation procedure

II.1. Sample preparation

The sediment sample “*Wasserhaltung 6, Becken 2*” is first thoroughly mixed using a mechanical mixing device and then sieved through a 500 mm mesh. The sediment sample is diluted with deionized water.

II. 2. Flocculation procedure (MWT05)

The goal of the lab testing consists in evaluating the flocculation and settling of the sediment samples using Omyased and phyllosilicate. The Omyased is diluted down to 10% TS with deionized water.

A constant target dosage of Omyased, per sludge total solid, as $\text{kg}_{\text{dry}} / \text{t}_{\text{TS}}$, is tested on a diluted sediment sample, while phyllosilicates are dosed, either one single phyllosilicat at different concentrations or several phyllosilicates at the same concentration.

The treated sediment sample is mixed for 2 minutes at 300 rpm after having dosed the required quantity of the Omyased into the sludge sample. The flocculation is then evaluated by observing the sludge flocculation over 20 minutes of settling time. The turbidity, respectively the clearness of the supernatant, is evaluated upon time in order to evaluate the turbidity decrease with time.

III. Results of the flocculation tests

III.1. Flocculation tests with surface-treated calcium carbonate (Omyased) alone

The testing is performed using the sediment sample “*Wasserhaltung 6, Becken 2*” that is sieved through a 500 mm mesh, and then diluted down to $\sim 2.5\%$ TS as already set out above.

The exact TS content is measured and used for the calculations of the Omyased dosage. The Omyased dosage is chosen according to previous lab testing showing good flocculation properties of the sediment sample “*Wasserhaltung 6, Becken 2*”, at $\sim 20 \text{ kg}_{\text{dry}} / \text{t}_{\text{TS}}$ of Omyased (Table 8).

It can be observed under these testing conditions that a flocculation takes place when using $\sim 20 \text{ kg}_{\text{dry}} / \text{t}_{\text{TS}}$ of Omyased, but a quite turbid supernatant is provided. After 20 minutes of settling time it can be observed that the flocculated sludge settled down to merely $\sim 40\%$ of the initial volume.

Table 8: MWT05 flocculation lab tests of sieved sample “*Wasserhaltung 6, Becken 2*” at 2.5% TS using Omyased alone at different dosages.

Dosage	20 minutes settling time	
Omyased (ppm)	Blank	500
phyllosilicate (ppm)		0
Omyased ($\text{kg}_{\text{dry}}/\text{t}_{\text{sed}}$)		19.6
phyllosilicate ($\text{kg}_{\text{dry}}/\text{t}_{\text{sed}}$)		0



Omyased
alone

III.2. Flocculation tests with phyllosilicate alone

The testing is performed using the sediment sample “Wasserhaltung 6, Becken 2” that is sieved through a 500 mm mesh, and then diluted down to ~ 2.5% TS as already set out above.

As phyllosilicate bentonite C2 sample alone is used. The phyllosilicate is added at different dosages between ~ 2 – 20 kg_{dry} / t_{TS} (Table 9).

It can be observed that the use of bentonite C2 alone is not providing any flocculation at all, at all the tested dosages. After 20 minutes settling time no flocculation has taken place, without any settling either.

Table 9: MWT05 flocculation lab tests of sieved sample “Wasserhaltung 6, Becken 2” at 2.5% TS using phyllosilicate alone at different dosages.

Dosage	20 minutes settling time					
Omyased (ppm)	Blank	0				
phyllosilicate (ppm)		0	50	100	250	500
Omyased (kg _{dry} /t _{sed})		0				
phyllosilicate (kg _{dry} /t _{sed})		0	2.0	3.9	9.8	19.6
phyllosilicate alone						

III.3. Flocculation tests with Omyased and phyllosilicate

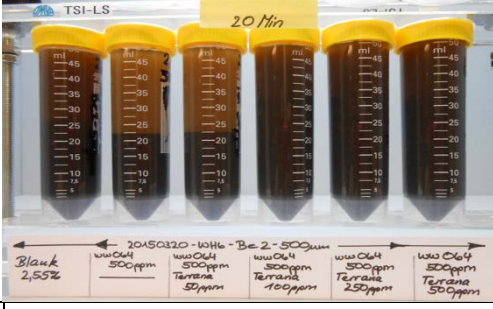
The testing is performed using the sediment sample “Wasserhaltung 6, Becken 2” that is sieved through a 500 mm mesh, and then diluted down to ~ 2.5% TS as already set out above.

The exact TS content is measured and used for the calculations of the Omyased / phyllosilicate dosages, added simultaneously. The Omyased dosage is chosen according to previous lab testing showing good flocculation properties of the sediment sample “Wasserhaltung 6, Becken 2”, at ~ 20 kg_{dry} / t_{TS} of Omyased (Table 10).

In the testing conditions it can be observed that the addition of the phyllosilicates Bentonil XR, Tixoton or Bentonite C2 provides clearer supernatants of the sediment sample, whereas

the addition of Terrana does not provide any improvement regarding either the quality of the obtained supernatants after flocculation or the final volume of the flocculated sludge.

Table 10: MWT05 flocculation lab tests of sieved sample “Wasserhaltung 6, Becken 2” at 2.5% TS using Omyased ($\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$) and different dosages of phyllosilicate.

Dosage		20 minutes settling time					
Omyased (ppm)	phyllosilicate (ppm)	Blank	500				
			0	50	100	250	500
			19.6				
			0	2.0	3.9	9.8	19.6
Omyased	Bentonite C2						
	Terrana						
	Bentonil XR						
	Tixoton						

III.4. Flocculation tests with calcium carbonate that has not been surface-treated and phyllosilicate

The testing is performed using the sediment sample “Wasserhaltung 6, Becken 2” that is sieved through a 500 mm mesh, and then diluted down to $\sim 2.5\%$ TS as already set out above.

As calcium carbonate a surface-modified calcium carbonate is used without surface-treatment (uncoated CC) and as phyllosilicate bentonite C2 is used. The calcium carbonate is used at a constant dosage of $\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ for the flocculation test, in combination with different dosages of phyllosilicate between $\sim 2 - 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ (Table 11).

Under these testing conditions it can be observed that the use of calcium carbonate without surface-treatment (no cationic polymer) alone or in combination with a phyllosilicate at different dosages is not providing any flocculation at all. After 20 minutes settling time no flocculation has taken place, without any settling either.

Table 11: MWT05 flocculation lab tests of sieved sample “Wasserhaltung 6, Becken 2” at 2.5% TS using calcium carbonate that has not been surface-treated ($\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$) and different dosages of phyllosilicate.

Dosage	20 minutes settling time					
Uncoated CC (ppm)	Blank	500				
phyllosilicate (ppm)		0	50	100	250	500
Uncoated CC ($\text{kg}_{\text{dry}}/t_{\text{sed}}$)		19.6				
phyllosilicate ($\text{kg}_{\text{dry}}/t_{\text{sed}}$)		0	2.0	3.9	9.8	19.6
Uncoated CC + phyllosilicate						

III.5. Flocculation tests Sequence (first surface-treated calcium carbonate and then phyllosilicate)

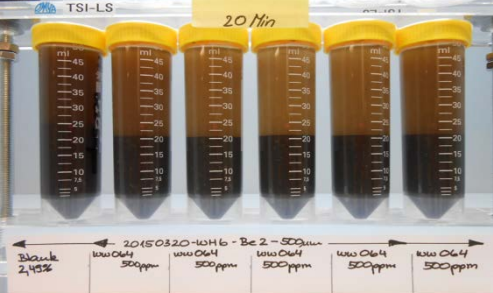
The testing is performed using the sediment sample “Wasserhaltung 6, Becken 2” that is sieved through a 500 mm mesh, and then diluted down to $\sim 2.5\%$ TS as already set out above.

Omyased is used as surface-treated calcium carbonate and bentonite C2 is used as phyllosilicate. First Omyased is added to the sediment sample at a constant dosage of $\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ and afterwards the phyllosilicate at different dosages between $\sim 2 - 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ is added (Table 12).

It can be observed that using first the surface-treated calcium carbonate and then the phyllosilicate does not provide any improvement regarding the clearness of the supernatants after the flocculation. The turbidity of the supernatant only decreases down to 269 NTU for the highest dosage of phyllosilicate for this sequence (first surface-treated calcium carbonate and then phyllosilicate).

The volume of the flocculated sludge obtained after the dosage of the phyllosilicate increases slightly from 40% of the initial volume when only the surface-treated calcium carbonate is added, to 55% of the initial volume for the highest dosage of phyllosilicate.

Table 12: MWT05 flocculation lab tests of sieved sample “Wasserhaltung 6, Becken 2” at 2.5% TS using first Omyased ($\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$) and afterwards different dosages of phyllosilicate.

Dosage	20 minutes settling time					
Omyased (ppm)	Blank	500				
phyllosilicate (ppm)		0	50	100	250	500
Omyased ($\text{kg}_{\text{dry}}/t_{\text{sed}}$)		19.6				
phyllosilicate ($\text{kg}_{\text{dry}}/t_{\text{sed}}$)		0	2.0	3.9	9.8	19.6
First Omyased alone						
First Omyased, afterwards phyllosilicate						
Final turbidity (NTU)	N/A	419	384	269	308	269
Flocculated sludge as volume ratio ($V_{\text{floc}}/V_{\text{initial}}$)	N/A	40%	40%	44%	45%	50%

III.6. Flocculation tests Sequence (first phyllosilicate and then surface-treated calcium carbonate)

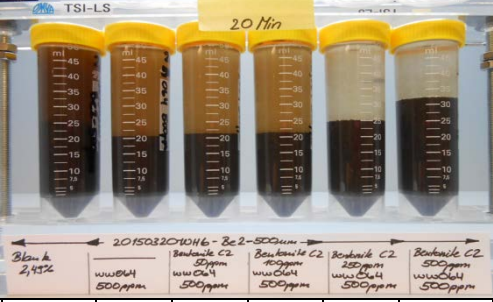
The testing was again performed using the sieved sediment sample “Wasserhaltung 6, Becken 2” that is diluted down to $\sim 2.5\%$ TS.

Omyased is used as surface-treated calcium carbonate and bentonite C2 is used as phyllosilicate. First the phyllosilicate is added to the sediment sample at different dosages of between $\sim 2 - 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ and afterwards Omyased is added at a constant dosage of $\sim 20 \text{ kg}_{\text{dry}} / t_{\text{TS}}$ (Table 13).

It can be observed that using the following sequence “first phyllosilicate and afterwards the surface-treated calcium carbonate” provides significant improvement regarding the clearness of the supernatants after the flocculation, when compared to the inverse sequence (see flocculation test III.5.). The turbidity of the supernatant decreased down to 77.8 NTU for the highest dosage of phyllosilicate for this sequence (first phyllosilicate and afterwards the surface-treated calcium carbonate), which is much lower than for the reverse sequence (first surface-treated calcium carbonate and then phyllosilicate).

The volume of the flocculated sludge obtained after the dosage of the phyllosilicate increases to a higher range, reaching 60% of the initial volume for the highest dosage of the phyllosilicate.

Table 13: MWT05 flocculation lab tests of sieved sample “Wasserhaltung 6, Becken 2” at 2.5% TS using first different dosages of phyllosilicate and afterwards Omyased (~20 kg_{dry} / t_{TS}).

Dosage	20 minutes settling time					
Omyased (ppm)	Blank	500				
phyllosilicate (ppm)		0	50	100	250	500
Omyased (kg _{dry} /t _{sed})		19.6				
phyllosilicate (kg _{dry} /t _{sed})		0	2.0	3.9	9.8	19.6
First phyllosilicate alone						
First phyllosilicate, afterwards Omyased						
Final turbidity (NTU)	N/A	396	341	332	115	77.8
Flocculated sludge as volume ratio (V _{floc} /V _{initial})	N/A	40%	40%	40%	50%	60%