Project name: | Purification of oil in water systems

Beamtime Report
27.08.2013 - 28.08.2013

General information

Name of the rapporteur	Name of the rapporteur's organisation
Tuomo Ritvanen	S.T. Ritvanen Oy
Type of research (nanotechnology/health care/chemistry etc.)	**Name of the research facility**
chemistry / environmental technology	MAX IV
Date of the measurement, duration	**Location of the event**
27.08.2013 - 28.08.2013, 16 hours	I711
Facility personnel participating in the measurement	
Dörthe Haase	

Description of the project

Research description (short summary as written in the application)
Spectroscopic methods suit to provide molecular-level data of processes, and their reaction products and intermediates that control overall reaction rates. We suggest that synchrotron based X-ray absorption spectroscopy (EXAFS and XANES) is performed at beamline I811, MAX-Lab. Company applies for 2 days for measurements. Particle size analysis (AFM) of sample are performed at University of Turku as part of the Science Link project. Samples: 1) particles before and 2) after use, and 3) soil sediment from the bottom of the cleaned water system. Also surface films of untreated (oily) water and treated water can be studied, if possible. The films can be studied without any pretreatment (acc. to D.B. Kleja et al., Chemical Geology 326–327 (2012) 19–26).
Summary of activities (experiments performed, beamtime used, preliminary overview of results, next steps and other relevant information)
Experiments performed: The samples where measured at the diffraction beam line I711 at MAX-Lab, MAX-IV laboratory, Lund, Sweden. The local responsible for the experiments at I711 was Dorthe Haase. Data treatment, phase identification, conclusions and report of diffraction data by Dorthe Haase. Beamtime used: 16 hours.

Preliminary overview of XRD results and next steps:

A short description from the company is that the samples are used as the active media in a water cleaning process. The material is exposed to dirty water together with some mechanical/electromechanical machine, in order to bind impurities dissolved in the water and hence clean a certain volume per time. The process itself is not clearly described here due to pending patent process.

To model the cleaning process, the different starting materials where exposed to both clean water and oily water for a certain time. The remaining probes of the active material where then measured, to map differences between the starting materials (hereafter called A, B, C and D) and their respective derivates that where exposed to clean water (hereafter marked by letter V) and oily water (hereafter marked with letter O).
The particles produced from the active material during the process where collected from the water by filtering and filled into capillaries. This is marked by the letter J.

Those modifications lead to the following list of measured samples:
A; AVJ; AOJ
B; BVJ; BOJ
C; CVJ; COJ
D; DVJ; The company could not provide sufficient sample of DOJ.

A = sample from starting material A
B = sample from starting material B
C = sample from starting material C
D = sample from starting material D
V = exposed to clean water
O = exposed to oily water
J = eroded material after process

All materials are natural materials that show the typical impurities expected for such raw materials.
Each sample was measured at 3 different spots and superimposed to minimise deviations in composition.

The diffractograms of all measured samples are shown (listed after samples) in the attachment.

experimental:
The sample capillaries where prepared by Dr. Taina Laiho from Materials Research Laboratory, Department of Physics and Astronomy, University of Turku
· untreated samples grinded to 75-125 µm
· samples that have been collected from water, gathered by filtering the water (AVJ)
· samples collected from oily water, gathered by filtering the water (AOJ)
The amount of DOJ was too small for analysis
The samples where measured at the diffraction beam line I711 at MAX-Lab, MAX-IV laboratory, Lund, Sweden, where the company gained access through the Science link project.

The local responsible for the experiments at I711 was Dorthe Haase. Data treatment, phase identification, conclusions and report of diffraction data by Dorthe Haase.

wavelength: ~ 12,5keV
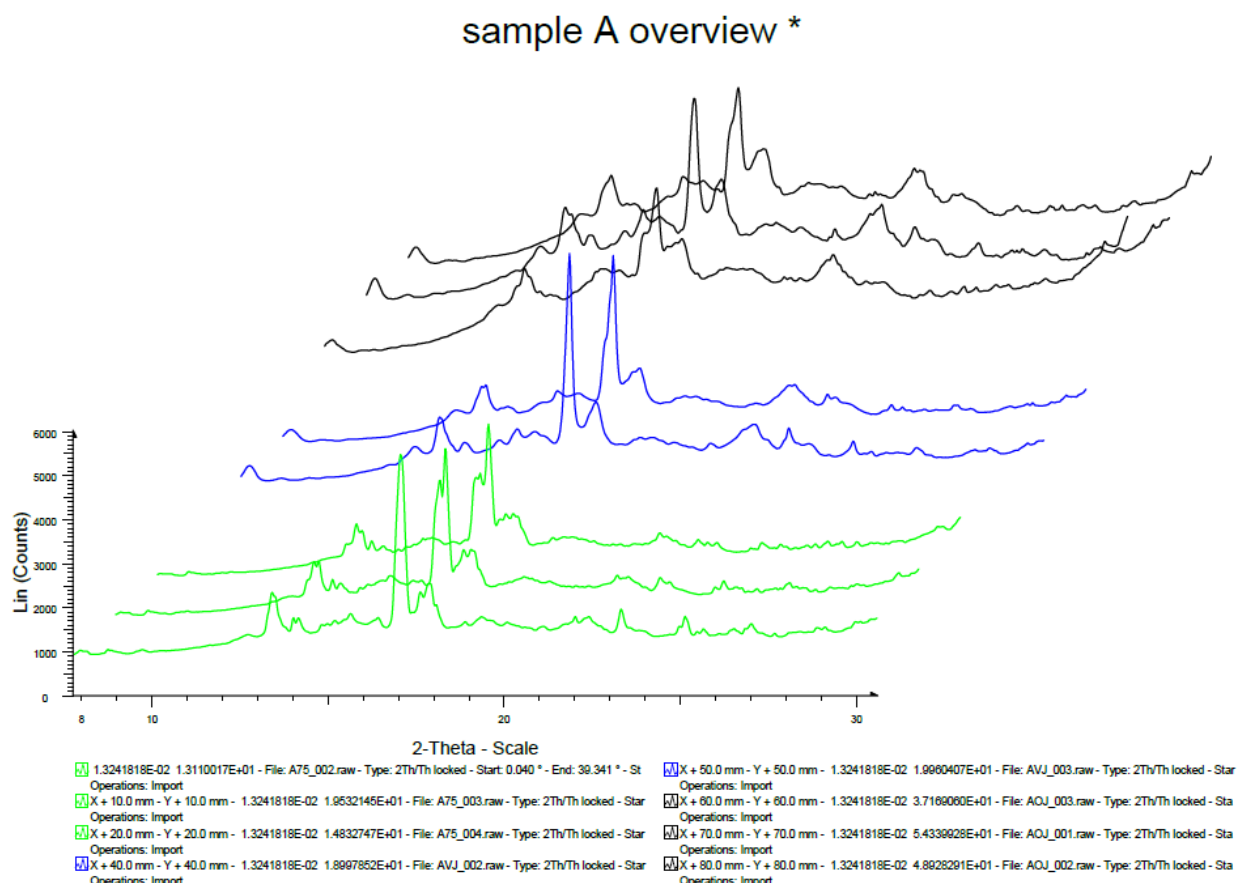sample-detector distance: ~ 100mm
detector: Oxford Diffraction Titan CCD (no binning)

Dissolution of crystalline materials in water is a process not yet clearly understood. Many groups in environmental chemistry and material science work with standard crystalline materials and/or mathematical modelling to gain insight in the complex processes that happen when those materials are exposed to water (see *Nov. 28 issue of the* Journal of Physical Chemistry C). Additional electro-mechanical treatment (Ritvanen method) would have to be considered in the modelling. As well reactions at the surface as in the bulk are examined and sample collection or preparation without interfering in the chemo-mechanical processes is challenging.
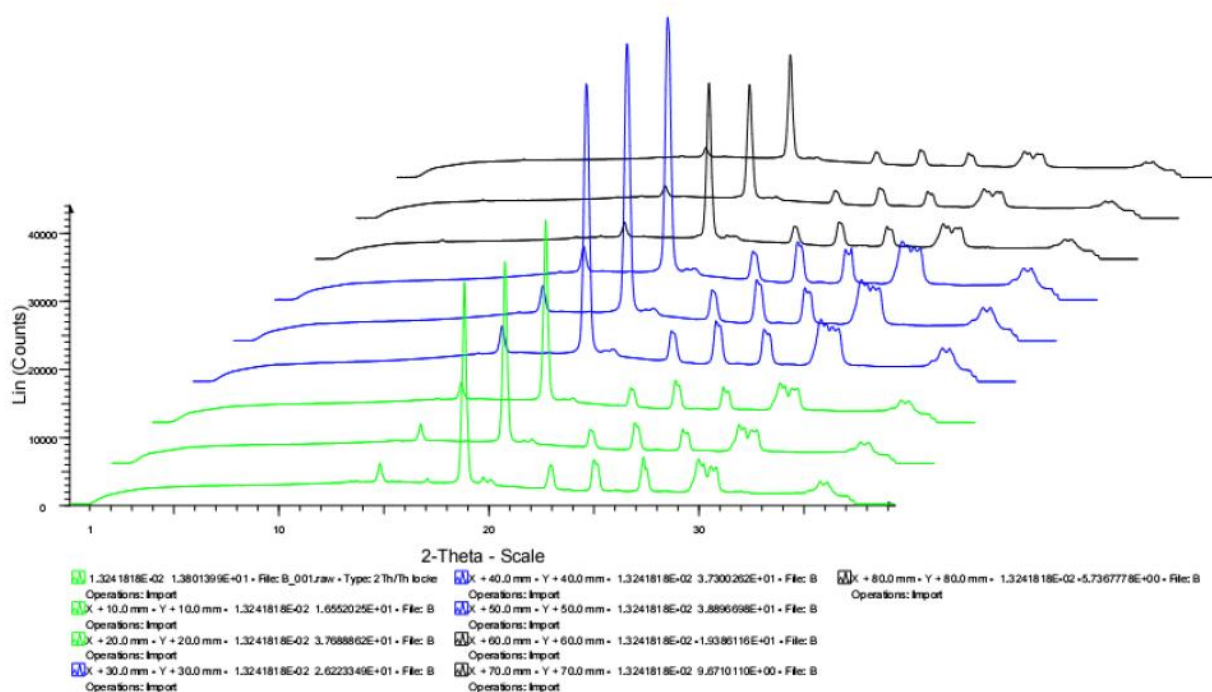
For the here described measurements, it was necessary to extract a very tiny amount of natural samples respectively to the treatment they have been through beforehand. Grinding of those materials adds further mechanical forces to the crystalline materials that need to be considered. The here measured samples are therefore definitely no model materials and one need to be reminded of the specific results gained from this experiments. However, one might be able to conclude on global mechanisms together with respective results from complement research methods (XPS).
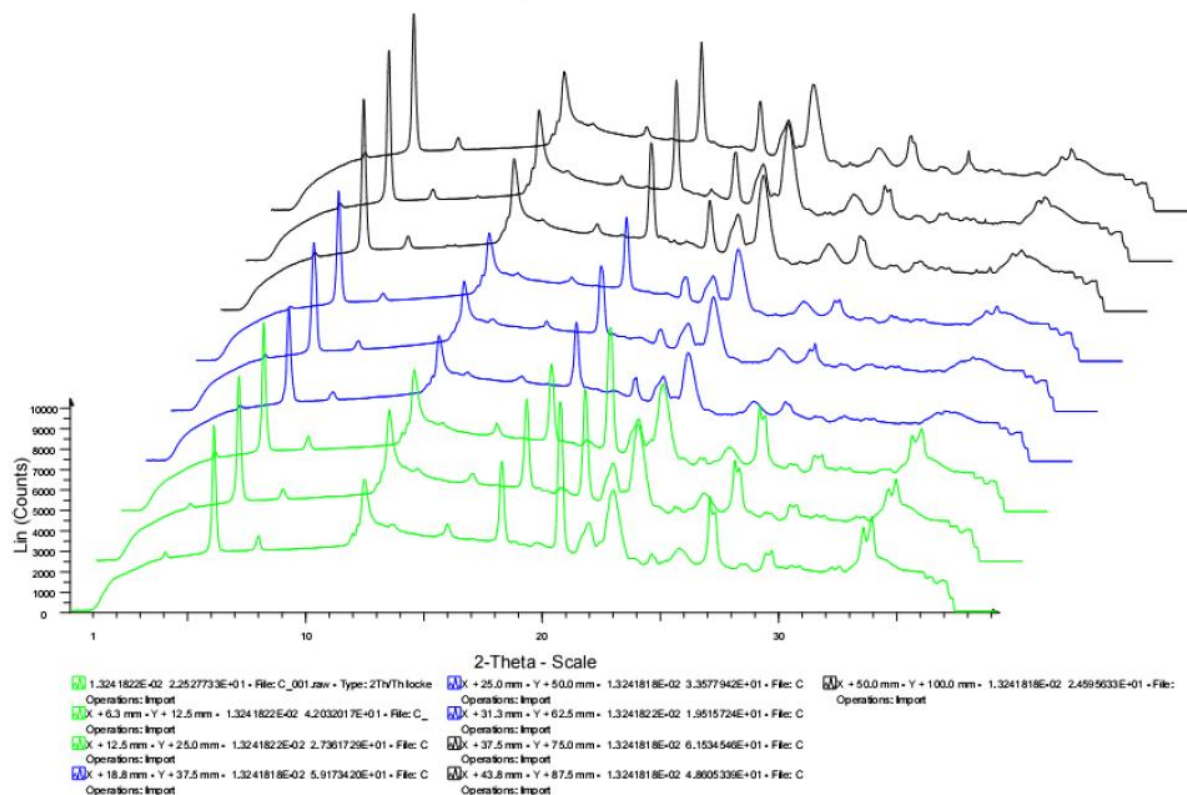
Results:
In all plots, the starting compound is plotted green, the compound exposed to clean water is plotted blue, and the compound exposed to oily water is plotted black. In the overview plots, all measured diffractograms are compared (* in sample A, one set of AVJ was removed due to error in measurement).
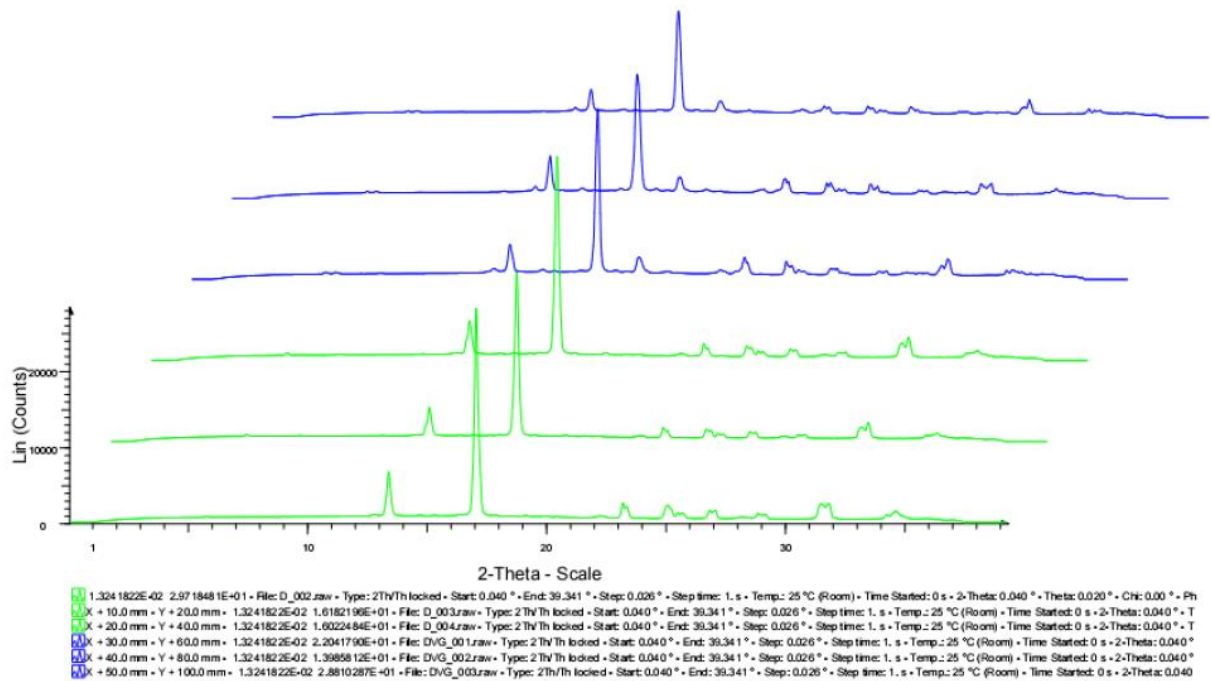
sample A overview *

1.3241818E-02 1.3110017E+01 - File: A75_002.raw - Type: 2Th/Th locked - Start: 0.040 ° - End: 39.341 ° - St Operations: Import
X + 10.0 mm - Y + 10.0 mm - 1.3241818E-02 1.9532145E+01 - File: A75_003.raw - Type: 2Th/Th locked - Star Operations: Import
X + 20.0 mm - Y + 20.0 mm - 1.3241818E-02 1.4832747E+01 - File: A75_004.raw - Type: 2Th/Th locked - Star Operations: Import
X + 40.0 mm - Y + 40.0 mm - 1.3241818E-02 1.8997852E+01 - File: AVJ_002.raw - Type: 2Th/Th locked - Star Operations: Import
X + 50.0 mm - Y + 50.0 mm - 1.3241818E-02 1.9960407E+01 - File: AVJ_003.raw - Type: 2Th/Th locked - Star Operations: Import
X + 60.0 mm - Y + 60.0 mm - 1.3241818E-02 3.7169060E+01 - File: AOJ_003.raw - Type: 2Th/Th locked - Sta Operations: Import
X + 70.0 mm - Y + 70.0 mm - 1.3241818E-02 5.4339928E+01 - File: AOJ_001.raw - Type: 2Th/Th locked - Sta Operations: Import
X + 80.0 mm - Y + 80.0 mm - 1.3241818E-02 4.8928291E+01 - File: AOJ_002.raw - Type: 2Th/Th locked - Sta Operations: Import
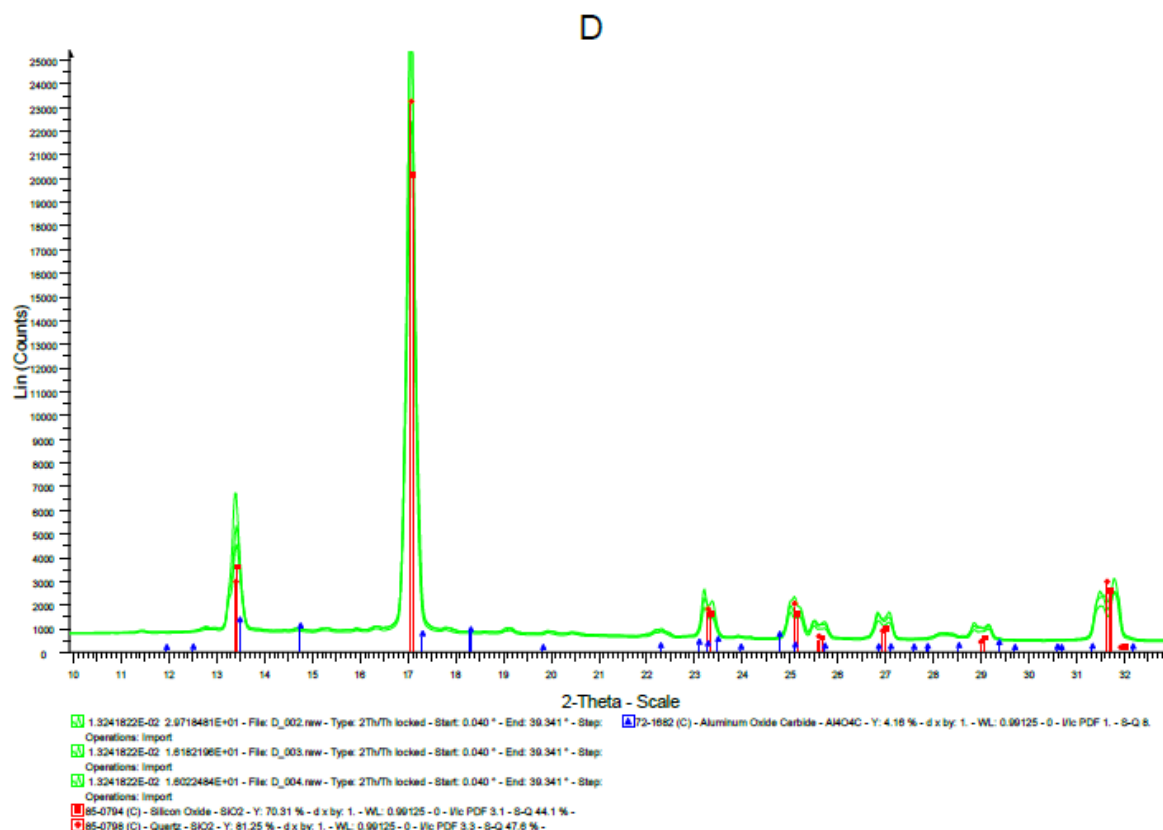
sample B overview

sample C overview

sample D overview

For phase identification, the respective samples where plotted together with the indentified phase peaks. The color code remains for the sample diffractograms, while the colors of the phases are chosen free with the main phases in red.

Example for a phase identification plot (sample D) :

D

Legend (below chart):
- 1.3241822E-02 2.9716481E+01 - File: D_002.raw - Type: 2Th/Th locked - Start: 0.040 ° - End: 39.341 ° - Step: Operations: Import
- 1.3241822E-02 1.6182196E+01 - File: D_003.raw - Type: 2Th/Th locked - Start: 0.040 ° - End: 39.341 ° - Step: Operations: Import
- 1.3241822E-02 1.6022484E+01 - File: D_004.raw - Type: 2Th/Th locked - Start: 0.040 ° - End: 39.341 ° - Step: Operations: Import
- 85-0794 (C) - Silicon Oxide - SiO2 - Y: 70.31 % - d x by: 1. - WL: 0.99125 - 0 - I/Ic PDF 3.1 - S-Q 44.1 % -
- 85-0798 (C) - Quartz - SiO2 - Y: 81.25 % - d x by: 1. - WL: 0.99125 - 0 - I/Ic PDF 3.3 - S-Q 47.6 % -
- 72-1882 (C) - Aluminum Oxide Carbide - Al4O4C - Y: 4.18 % - d x by: 1. - WL: 0.99125 - 0 - I/Ic PDF 1. - S-Q 8.

Conclusions:

All investigated materials are natural and no synthetic component could be indentified. Since the powder-XRD method only gives results for crystalline materials and can not identify most organic compounds (except crystalline), the conclusions are founded on the changes of crystalline phases during treatment.

The sample **A** is composed of several different crystal phases (aluminosilicates like KAlSi3O8 – NaAlSi3O8 – CaAl2Si2O8, too complex and overlapping for reliable crystal phase analysis). It mainly maintains its chemistry during the process. The occurring changes are suspected to represent the versatility of the sample type. However, the increase of carbon rich structures in AVJ and AOJ might point towards carbon bonding within crystal structures. Due to the limited amount of time the samples is exposed to waste water, this would only be possible on the outer layer of crystallites (surface). Crystallite size and microstrain show an effect of mechanical stress. It is concluded that the bulk materials chemistry is not changing for this sample.

Sample **B** also seems to maintain its chemistry during the process. The main component of sample B is Calcite (CaCO3) but also varieties occur, where the Calcium is replaced by Magnesium and hence revealing minerals with different Ca/Mg content (Huntite, Dolomite etc.). Those minerals exhibit minor changes after the respective treatment. Even here slight increase of carbon rich compounds. Crystallite size and microstrain exhibit minor changes. We conclude the bulk materials chemistry is not changing for this sample.

Sample **C** has MgSi4O10(OH)2 (Talc) as main component. The microstrain of this material shows strong effects after being exposed to the process. Although the chemistry of the sample exhibits similar small changes regarding the main chemistry (only slight increase in carbon containing crystals), the macroscopic structure of the crystallites changes a lot, giving rise to different particle shapes and hence showing preferred orientation in respective grades.

Sample **D**, a silicon oxide with accompanied phases, shows additional phase of Calcite ($CaCO_3$) and nitrides (carbon nitride and silicon aluminium nitride) after being exposed to water. It is expected that those compounds do not form out of the starting compound, but are found in the water and bond to the surface of the crystals. An overnight in-situ test of exposing sample D to clean (deionised) water did not show any change of the structure.

Note:
Organic compounds (from waste water), physically attached at the surface of crystallites can not be observed with this method.
But together with the XPS results from the same samples, one could conclude a mechanical binding of the impurity materials on the crystalline surfaces. If kept long enough under equilibrium conditions, structural changes might occur.

Continuation:
It is suggested to continue testing those materials (and method) with additional X-Ray techniques, like SAXS and/or EXAFS. BET surface analysis of the material before and after treatment would also give an insight of the active surface and its influence of chemical/physical reactivity.

In addition to XRD method, which gives structural information of samples, also XPS for chemical analysis was performed. The XPS spectra of the samples were measured at the University of Turku. The measurements were performed and the XPS data was analysed by Taina Laiho.

Preliminary overview of XPS results and next steps:

SAMPLE A

Atomic concentrations measured from mineral A samples (A, AVJ and AOJ). It is possible that other elements are present in low concentrations beyond the limit of detectability of this method.

element	concentration (atomic-%)		
	A	AVJ	AOJ
C	10,72	17,63	17,92
O	61,10	57,07	56,46
Si	17,40	13,98	13,31
Al	7,21	7,88	7,94
Fe	1,26	1,71	1,81
Na	0,94	0,35	0,18
K	0,89	0,51	0,94
Ca	0,47	0,69	0,55
N	0	0,19	0,74
F	0	0	0,17

Elemental composition of samples does not change markedly during the process. Amount of carbon in samples AVJ and AOJ is about doubled from the amount of carbon in sample A. Also amount of oxygen has increased if not the absolute value, but the ratio O/Si, is studied. This may indicate gathering of organic compounds on the surface of eroded or precipitated mineral particles. Water and oily water treated samples (AVJ and AOJ) also contain small amount of nitrogen probably originating from air.

Amount of Si seems to decrease, but surface adsorption of organic compounds 'hide' the mineral inside the particles, since XPS method is very surface sensitive. Amount of aluminum and iron may have increased a little. Sodium decreases.

Sample AOJ contains Fluorine. It is suspected to originate from oil, since there is no fluorine in samples A or AVJ.

SAMPLE B

Atomic concentrations measured from mineral B samples (B, BVJ and BOJ). It is possible that other elements are present in low concentrations beyond the limit of detectability of this method.

element	concentration (atomic-%)		
	B	BVJ	BOJ
C	32,01	35,31	35,79
O	52,23	50,57	49,72
Ca	12,51	12,69	12,35
Si	1,42	0,81	1,03
Mg	0,65	0,26	0,55
Al	0,56	0,29	0,20
Na	0,28	0	0
Cl	0,27	0,03	0,03
S	0,03	0,04	0,08
F	0,03	0	0,15
N	0	0	0,09

Amount of carbon has increased as a result of water or oily water treatment, but not much. According to XPS results relative amount of carbonate type carbon and other carbon does not change. Amount of oxygen has decreased a little, but not markedly. Calcium citrate $Ca_3(C_6H_5O_7)_2$ or calcium acetate monohydrate ($Ca(CH_3COO)_2·H_2O$) may have formed on to the mineral surface, but there is no evidence of that seen in the spectra.

Amount of calcium in the samples remains about constant. According to the literature it is supposed that Ca^{2+} ions could be precipitated to the surface, but process may have removed them. [L. Eisenlohr, K. Metveva, F. Gabrovšek and W. Dreybrodt, The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous $H_2O–CO_2$ solutions, Geochimica et Cosmochimica Acta, Vol. 63, No. 7/8, pp. 989–1002, 1999.]

Silicon has been found in low amount indicating the presence of Si containing minorities in the material. It is supposed that some nano-complexes are incorporated into the sample B matrix giving 'extra' elements to the elemental concentration list. Keeping in mind that the growth of calcite proceeds in an environment where the presence of aluminosilicates is ubiquitous and the growth of large perfect calcite crystals is unlikely, it may be plausible that nanocomplexes might be incorporated in a highly disturbed lattice. [L. Eisenlohr, K. Metveva, F. Gabrovšek and W. Dreybrodt, The inhibiting action of intrinsic impurities in natural calcium carbonate minerals to their dissolution kinetics in aqueous $H_2O–CO_2$ solutions, Geochimica et Cosmochimica Acta, Vol. 63, No. 7/8, pp. 989–1002, 1999.] Si, Mg, Al and Na are typical elements in aluminosilicates. Relative amounts Si/Ca, Mg/Ca, Al/Ca and Na/Ca are higher in case of original material B and lower in a materials BVJ and BOJ gathered from solution. This may indicate that aluminosilicate nano-complexes, which are incorporated in the calcite matrix, are dissolved or eroded from the surface less than $CaCO_3$.

XPS results indicate increase of F in material that has been collected from oily water. The formation of fluorite (CaF_2) on the sample B surface has been noticed earlier due to the reaction of free Ca^{2+} produced by dissolution of sample in presence of acid, adsorption of fluoride on sample or due to penetration by fluoride slightly into the sample. Also in-situ

generation of Ca^{2+} ions in crushed sample column by passing CO_2 through the sample column can reduce the fluoride level in water. Calcium hydroxide ($Ca(OH)_2$) is used for separation of fluoride from drinking water. Calcium chloride ($CaCl_2$) and calcium sulphate ($CaSO_4$) are used in treatment of industrial waste water containing fluoride. [S.K. Nath, S. Bordoloi and R.K. Dutta, Effect of acid on morphology of calcite during acid enhanced defluoridation, Journal of Fluorine Chemistry 132 (2011) 19–26.]

Small amount of sulfur is seen in the spectra. Sample is reacting with sulfate (SO_4^{2-}) in acidic environment with water giving gypsum in solid form. [A.J. Toprac, G.T. Rochelle, Limestone dissolution in stack gas desulfurization, Environ Prog 1 (1982) 52–58.]

Small amount of nitrogen is seen in the spectrum that has been measured from the oily water treated sample.
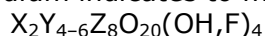
SAMPLE C

Atomic concentrations measured from mineral C samples (C, CVJ and COJ). It is possible that other elements are present in low concentrations beyond the limit of detectability of this method.

element	concentration (atomic-%)		
	C	CVJ	COJ
C	10,52	16,67	13,13
O	58,97	55,26	56,56
Si	15,78	14,36	15,97
Mg	8,30	7,13	7,75
Al	5,56	5,00	5,34
Fe	0,63	0,90	0,65
N	0	0,61	0,34
Ca	0,04	0,06	0,11
Na	0,20	0,01	0,15

Main component of sample C is talc, $MgSi_4O_{10}(OH)_2$. Relatively high atomic-% of magnesium in comparison to silicon and the presence of aluminium indicate the presence of other minerals in addition to talc.

Ca may originate from amphiboles, such as tremolite-actinolite having a chemical formula $Ca_2Mg_5Si_8O_{22}(OH)_2$ and/or $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$. It may also originate from mica. Also sodium indicates to mica. Chemically, micas can be given the general formula
    $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$
        in which X is K, Na, or Ca or less commonly Ba, Rb, or Cs;
        Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.;
        Z is chiefly Si or Al, but also may include Fe^{3+} or Ti.
Structurally, micas can be classed as dioctahedral (Y = 4) and trioctahedral (Y = 6). If the X ion is K or Na, the mica is a "common" mica, whereas if the X ion is Ca, the mica is classed as a "brittle" mica. [wikipedia]

One can see from the atomic concentrations that particles that have been collected from water (CVJ) or oily water (COJ) contain more carbon than untreated sample C. Also nitrogen can be found from the water or oily water treated particles. Otherwise the elemental composition of samples has not changed. Amount of oxygen is no markedly different. In this case no fluorine is detected in the sample gathered from oily water.

SAMPLE D

Atomic concentrations measured from mineral D samples (D and DVJ). It is possible that other elements are present in low concentrations beyond the limit of detectability of this method.

| element | concentration (atomic-%) | |
	D	DVJ
C	18,17	29,43
O	56,44	48,18
Si	21,80	19,03
Al	2,68	1,92
K	0,48	0
Na	0,27	0
Ca	0,16	0,55
N	0	0,59
Zn	0	0,31

Atomic concentrations are typical for natural quartz. XPS results of sample D show ratio Ca/Si = 0,0073 and for sample DVJ (dust collected from water at the end of experiment) Ca/Si = 0,029. These values indicate that during the process silica SiO_2 has dissolved from the original material and Ca concentration of the material has increased. It may be, that tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O$) or xonotlite ($Ca_6Si_6O_{17}(OH)_2$) have formed during the process.

The quartz-water system can be governed by the following equation. It is a simple surface reaction to form silicic acid monomer, otherwise called dissolved silica: $2H_2O$ (l) + SiO_2 (s) ⇔ H_4SiO_4 (aq). Many examples of silica dissolution within deeply buried quartz sandstones can be found in the literature. [G. S. Kumar, A. Ghassemi, Numerical modeling of non-isothermal quartz dissolution/precipitation in a coupled fracture–matrix system, Geothermics 34 (2005) 411–439.]

SUGGESTIONS FOR FUTURE STUDIES

These laboratory experiments were done in a short time-scale. Field experiments should be done in addition to laboratory experiments.

Changes of elemental composition of minerals during the process should be measured with a more accurate method. Produced and precipitated material should be collected from water and analysed. Probably XRF could give useful results.

The water sample should be studied to measure concentrations of dissolved material with for example with ICP-AES.

How would you describe cooperation and assistance from industrial liaison officers and national contact points while preparing and carrying out the research at large scale facilities?

Cooperation with national contact points was well organized. Contacts had personal experience from such studies and understood the needs of company. Company gained sufficient assistance for application at time and help with preparing for studies.
As the company hadn't knowledge of synchrotron based methods one would had needed more diverse presentation of possibilities and restrictions of available methods from industrial liaison officers before studies.

Other personal remarks

Studies and cooperation revealed new opportunities in research for company. We are looking forward to an additional cooperation with Universities in future.

Annexes

Annexes
(list of annexes; meeting minutes, graphical illustrations, tables and other supplementary data)

Figure 1: Synchrotron Small Angle X-ray Scattering facility
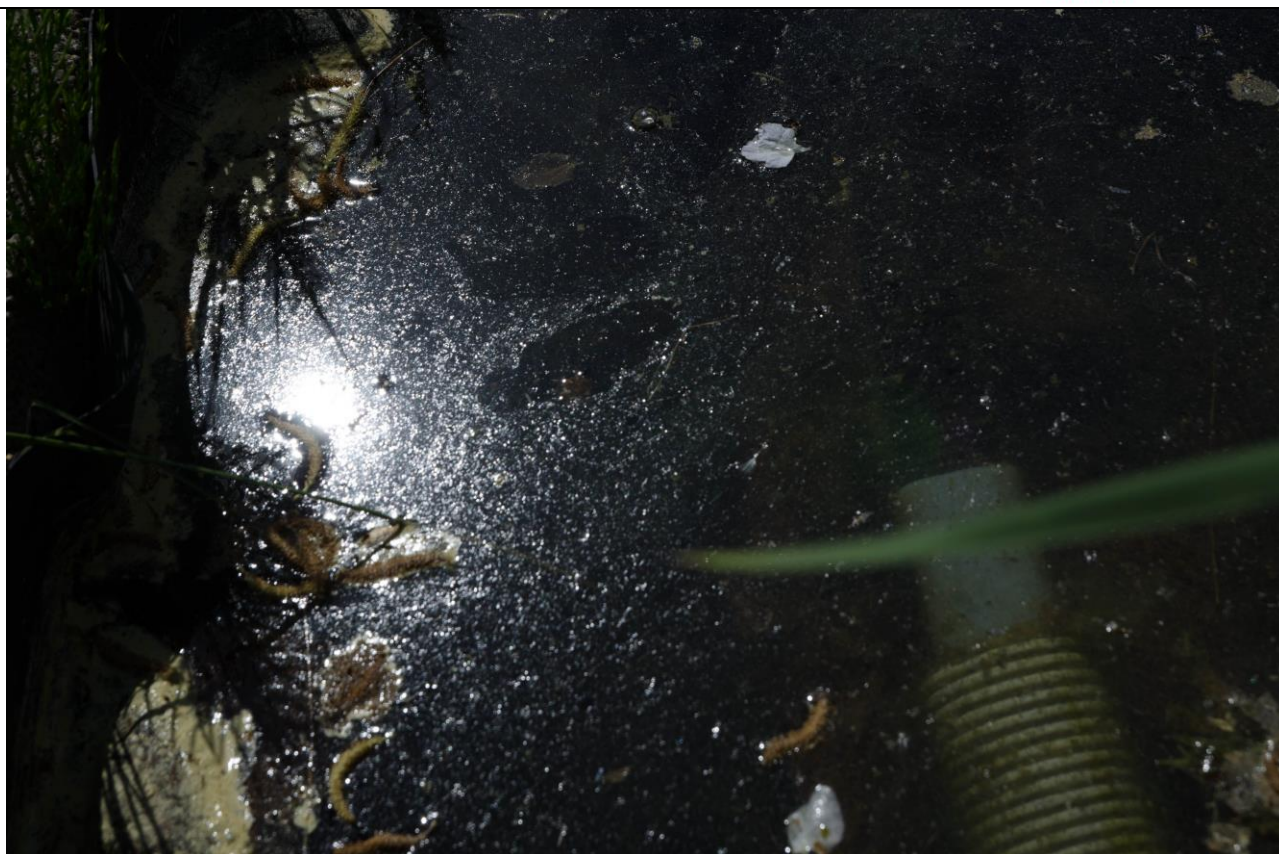Figure 2: Fieldtest Oil etc film removal from naturalwatersystem
Figure 2: Feasibilitytest Industrial wastewater purification testfacility (sulphuric acid neutralization)
Figure 3: Feasibilitytest Comparison to traditional precipitation method (pickling proses)
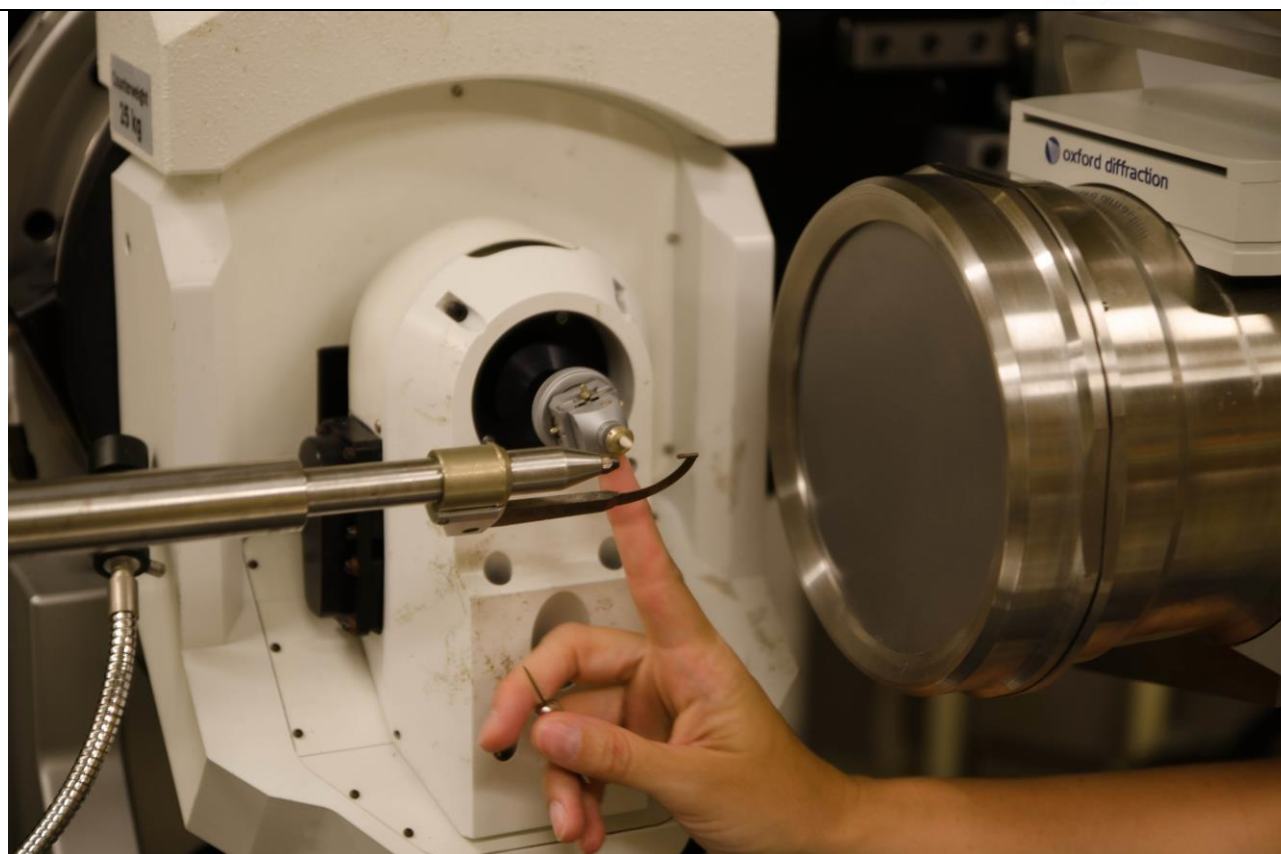
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