Equilibria and Kinetics of Flotation Chemical Sorption Reactions in Tailings-Seawater Systems

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ABSTRACT

Submarine tailings placements (STPs) is a viable alternative to land-based waste disposal. The potential environmental impacts of STPs are the results of oceanographic, biochemical, ecological conditions of the site, while the technical conditions of mineral processing has the incredible importance. In order to justify the application of STPs it is crucial to evaluate the tailings as non-toxic materials at the point of disposal. The properties of the tailings are affected by comminution and separation processes, but there is a considerable potential for improving these characteristics through novel approaches to dewatering and flocculation, as well as the recycling of process water and process chemicals. When collector molecules bound to a mineral surface by physical adsorption and exposed to seawater with its much higher ionic strength, significant desorption can occur (Schwarzenbach et al., 2003). By investigating the desorption characteristics of the adsorbed collectors, important information regarding their mobility could be obtained and facilitate improved solutions for chemical recycling or immobilisation. By using a second thickening step, a significant amount of the dissolved collector could be concentrated in a relatively small volume. In process plants where both flotation tailings and 'chemically unpolluted' tailings are available, the latter might be used a solid reagent to immobilise the chemicals desorbed from the former.

In the present study the equilibria and kinetics of flotation chemical sorption reactions in tailings-seawater systems, as series of adsorption / desorption have been performed for the esterquats-containing collector FLOT 2015 and the calcite-silicates mineral systems. As part of this work, simple and robust analysis procedures have been developed based on a UV spectroscopy. Combined with techniques for direct characterisation of surface adsorbed species, this methodology offers new insight into the faith of flotation chemicals when the tailings are exposed to seawater.

INTRODUCTION

Currently the growing demand for mineral resources followed by the enormous increase in mining activity create the need for disposal of the large amount of tailings. Submarine tailings placements (STPs) is a viable alternative to land-based waste disposal (Dold, 2014; Ramirez-Llodra, 2015). The potential environmental impacts of STPs are the results of the oceanographic, biochemical and ecological conditions of the site, as well as the conditions resulting from mineral processing. The physiochemical properties of the tailings are governed by the preceding comminution and separation processes, but there is a considerable potential for improving these characteristics through novel approaches to dewatering and flocculation, as well as the recycling of process water and process chemicals. These are established unit operations, but they are not necessarily optimised for the reactions and interactions that take place in a system where fresh process water meets seawater. When collector molecules bound to a mineral surface by physical adsorption are exposed to seawater with its much higher ionic strength, significant desorption can occur. By investigating the desorption characteristics of the adsorbed collectors, important information regarding their mobility could be obtained which would be valuable for environmental impact assessment.

In Norway, legislation has spurred a replacement of reagents towards more environmentally friendly alternatives. Hence, Omya Hustadmarmor AS is now using the esterquats-containing reagent FLOT 2015 as a cationic collector in reverse flotation to remove silicates from calcite. Esterquats are cationic surfactants with the ester bond located between the quaternary ammonium group and the long hydrocarbon chain, and can be decomposed into non-surface-active fragments through a base-catalysed hydrolysis process (Rubingh & Holland, 1992; Hellberga et al., 2000; Overkempe et al., 2005) and provide easy final degradation into inorganic products such as carbon dioxide, water and mineral salts (Swisher, 1987; Federle et al., 1997; Para et al., 2015; Kronberg et al., 2017). However, due to the complexity of the reagent and stability in aqueous solutions in the limited pH range for the certain period of time, FLOT 2015 does not appear to have been extensively tested with regard to chemical properties and quantification of the main components in aqueous medium, especially in seawater systems. Thus, it has become imperative to evaluate a simple and adequate method for determination of esterquats-containing reagent FLOT 2015 and build the successful testing schemes for its quantitative analysis in the marine environment.

Spectroscopic methods have been intensively used for surfactants analysis in aqueous medium (Bassarab et al., 2011; Wulf et al., 2010, Zhang et al., 2015). A UV spectrophotometry is a widely accepted method for detection and quantitative measurements of esterquats due to simplicity, rapidity and portability. Currently, there are several methodologies validated for individual esterquats based on methyl orange compounds (El-Khateeb & Abdel-Moety, 1988; Bonilla Simon et al., 1990), bromothymol blue (Yamamoto & Motomizu, 1991), bromocresol series dyes (Motomizu et al., 1992). However, in a multicomponent system, the analysis becomes more challenging.

In the present study the equilibria and kinetics of flotation chemical sorption reactions in tailings-seawater systems, as series of adsorption/desorption have been performed for the esterquats-

containing reagent FLOT 2015 and the calcite-silicates mineral samples. As part of this work, simple and robust analysis procedures have been developed based on a UV spectrophotometry.

METHODOLOGY

Apparatus

All absorption spectra were made using a HACH-Lange UV spectrometer (DR 3900) (USA), equipped with rounded cuvettes. A Metrohm AG pH-meter instrument (913 pH) (Switzerland) was used for measuring the pH values in the solutions and mineral suspensions.

Materials

Bromocresol Purple (BCP) and chloroform were purchased from Sigma Aldrich Co., Schnelldorf, Germany. The flotation collector FLOT 2015 was obtained from Omya Hustadmarmor AS, Elnesvågen, Norway. The molecular formulas of three main components of FLOT 2015 are listed in Table 1.

Table 1 Molecular formulas of the main components of FLOT 2015

Name	Molecular formula
tris (2-hydroxyethyl) (methyl) azanium (QAC)	$C_7H_{18}NO_3$
bis(2-hydroxyethyl)(methyl){2-[(15E)-octadec-15-enoyloxy]ethyl} azanium (monoester)	$C_{25}H_{50}NO_4$
(2-hydroxyethyl)(methyl)bi {2-[(15E)-octadec-15-enoyloxy]ethyl} azanium (diester)	$C_{43}H_{82}NO_5$

Phosphate buffer solution (0.1 M) was used to adjust the pH of reaction solutions to 7.1. All single chemicals were of analytical-reagent grade and used without further purification. Artificial seawater was prepared according to the procedure (Kesler et al, 1967). Table 2 shows the chemical composition of calcite-silicate samples obtained from Omya Hustadmarmor AS, Elnesvågen, Norway. The sample consisted of approximately 95% calcite and minor amounts of silicates and graphite.

Table 2 Chemical composition of the calcite-silicates sample, %

Fe_2O_3	TiO_2	CaO	K_2O	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	MnO_2	LOI
0.64	0.01	54.76	0.01	0.01	0.44	0.03	1.08	0.02	0.22	42.38

Methods

Stock and standard solution preparation

The BCP stock standard solution $1.25 \cdot 10^{-4}$ M was prepared by dissolving accurately weighed amounts of the dye in 10 mL of 0.01 M sodium hydroxide solution and diluting to 100 mL with distilled water. A stock solution of FLOT 2015 was prepared by dissolving 1 g of the reagent in the acidic water

solution and then made up 1000 mL to obtain pH 5.0. Aliquots of stock solution (1g/L) were transferred into a set of 25 mL flasks and volumes were completed to the mark with distilled water to produce solutions in the concentration range 0.5-60 mg/L.

Quantitative analysis

The quantitative analysis was conducted by thoroughly mixing 25 mL of FLOT 2015 solution, 2.5 mL of buffer solution, 2 mL of BCP solution and 8 mL of chloroform in a 70-mL plastic bottle for 2 min. The phases were allowed to separate for 5 min. using a Pasteur pipette an aliquot (4 mL) of the chloroform layer was removed and placed in a clean cuvette. The absorption spectra of samples were measured at 380 nm against a blank chloroform sample. Calibration graphs were constructed by plotting absorbance of the chloroform layer against the concentration of FLOT 2015 in distilled water.

Adsorption/desorption tests

Adsorption tests were conducted in 70 mL plastic bottles, each using 1 g of sample in 30 mL of reagent solution. The suspension was agitated for 10 min, centrifuged for 10 min and subsequently filtered. For desorption tests the mineral sample with adsorbed FLOT 2015 was mixed with 30 mL of artificial seawater for 20 min to desorb the collector, centrifuged for 10 min and filtered using the syringe with 0.45 micron filter. Then according to the quantitative analysis procedure 25 mL of the filtrate was transferred into the clean 70-mL plastic bottle and examined for FLOT 2015 determination. For kinetics desorption experiments the retention time values were 10, 20, 30 min, 1, 2, 3, 5, 10, 18, 24 hours and 10 days.

RESULTS AND DISCUSSION

Validation of the proposed UV- spectrophotometric method

We propose a simple, rapid and low cost method for analysis of esterquats-containing reagents based on the formation of an ion pair between a cationic collector and an anionic dye. When the cationic collector, namely FLOT 2015, is introduced to the anionic dye solution, the solvent rearrangement around free ions leads to ion pair formation (Roy et al., 2017). This results in a change in absorbance, observed as a decrease in intensity of the dye colour. The ion pair complex is extractible into an organic solvent, while the dye alone is not, so the intensity of the organic phase colour is directly proportional to the esterquat concentration (Water & Kupfer, 1976; Schmitt, 2001).

The developed method showed that the buffer solution of pH 7.1 gave the maximum colour intensity, stability of colour and highest absorbance value using BCP after chloroform extraction with reproducible results at wavelength of 380 nm. The proposed method showed linearity in the range of 0.5-60 mg/L with a correlation coefficient of 0.9820. Standard and relative standard deviation

obtained by intra- and inter-day precision tests of the proposed method were within the permissible bias range and considered satisfactory.

Adsorption/desorption studies

To verify the relationships between the concentration of FLOT 2015 and the level of its adsorption, a series of tests were set up to determine adsorption capacity of the reagent on the calcite-silicates samples. The concentration of FLOT 2015 at equilibrium (c_{eq}) was measured and the adsorption capacity was calculated by the equation:

$$A = \frac{(c_i - c_{eq})V}{m} \tag{1}$$

where c_i-initial concentration of FLOT 2015 in the solution (mg/L), c_{eq} – concentration of FLOT 2015 at equilibrium in the solution (mg/L), V-volume of the solution (L), m- mass of the sample (g).

The adsorption capacity was rapidly increased with the increasing concentration of FLOT 2015 and then slowed down when the concentration reached 30 mg/L. This stabilization was caused by the recognition sites on the mineral sample which were almost completely occupied by FLOT 2015 when exceeding the equilibrium concentration. The adsorbed amount of FLOT 2015 on the mineral also increased with increasing contact time and remained almost constant when the equilibrium condition was established. The optimum agitation time for adsorption experiments was investigated from 1 to 20 min at ambient temperature ($20 \pm 2°C$). A retention time equal to 10 min was optimal. To illustrate the value of adsorption the adsorption isotherm was plotted. Figure 1 shows the adsorption capacity via concentration of FLOT 2015 at the equilibrium in the solution before and after mixing with seawater.

The shape of the curves were fitted to the adsorption isotherm Type IV (Brunauer et al., 1938; Kruk & Jaroniec, 2001) and depicted to the mostly monolayer-multilayer adsorption. The linear part at the beginning indicated the stage when the adsorption was started. The intermediate flat region corresponded to monolayer formation followed by multilayer. At the initial FLOT 2015 concentration of 35 mg/L the monolayer was almost complete and the multilayer began to form. The steepness of the isotherm indicated the hysteresis and was usually attributed to the thermodynamic effect. It was proposed that most probably there were particles with internal voids of irregular shape. When desorption studies were undertaken hysteresis effects were also observed. No significant desorption was observed up to 45-60 mg/L by mixing with seawater for 10 and 60 min. This phenomenon can be described as slow reversible or even resistant sorption. Also, this indicates the relative stability of the monolayer of FLOT 2015 on the mineral surface with FLOT 2015 concentration equal to 30-35 mg/L while the second layer can be removed when the concentration exceeds 45 mg/L. It was noticed that desorption of FLOT 2015 by seawater was highly dependent on time. Thus, the residence time was evaluated via kinetic experiments at pH 8.5, obtained after introducing the mineral sample in seawater. Figure 2 shows the effect of time on FLOT 2015 desorption by seawater resulting in a change

of FLOT 2015 desorbability (the percentage of desorbed FLOT 2015 with regards to the total initially adsorbed FLOT 2015).
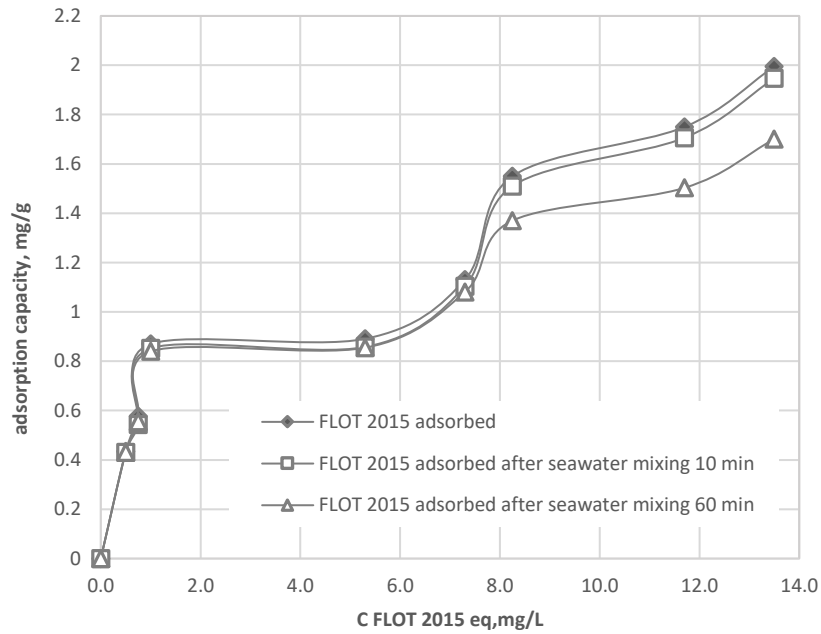
Figure 1 Adsorption/ desorption behavior of FLOT 2015 on the calcite-silicates mineral system
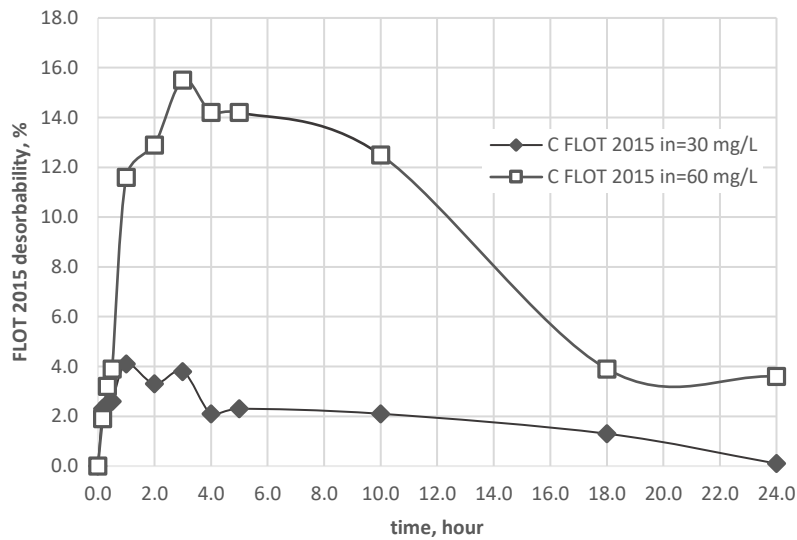
Figure 2 Kinetics of FLOT 2015 desorption from the calcite-silicates sample by seawater

It is obvious that desorption of FLOT 2015 by seawater increases considerably when the retention time is extended up to 3 hours. The desorption capacity increases from 2.3 up to 3.8% and from 1.9 up to 15.5% with FLOT 2015 initial concentration of 30 and 60 mg/L, respectively. Further increase in time does not strongly effect on the change in desorption up to 5 hours and the saturation point has been reached. Apparently, FLOT 2015 desorbs more readily from the mineral sample with the larger initial concentration of the solution (60 mg/L). It can be explained by desorption from multiple layers of FLOT 2015 at the higher concentration whereas the lower value tends to form only a monolayer on the mineral surface which is stable at the current conditions. There is no big difference between the 30 mg/L and 60 mg/L concentrations with respect to the trend of the desorption curves. Moreover, the storage of the sample for 18-24 hours leads to the decrease in FLOT 2015 detection by the UV-method. As previously discussed, esterquats possess at least one ester group and are readily biodegradable as 80% of the theoretical carbon dioxide within 28 days. Degradation in sewage water systems took place with a half-life of 8-10 hours. This is probably the general explanation of FLOT 2015 behaviour in seawater storage for more than 18-24 hours.

CONCLUSION

A rapid, robust and portable UV- spectrophotometric method was validated and proposed for successful measurement of FLOT 2015 quantitatively in distilled water and seawater. Our research found that this method could provide simple and low cost analysis of FLOT 2015 with relatively high sensitivity. By investigating the desorption characteristics of FLOT 2015 adsorbed, important information regarding its mobility was obtained. It was obvious that as the concentration of FLOT 2015 increased the desorption by seawater became faster and more significant. Combined with techniques for direct characterisation of surface adsorbed species, this methodology offers new insight into the faith of flotation chemicals when the tailings are exposed to seawater.

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REFERENCES

Bassarab, P., Williams, D., Dean, J.R., Ludkin, E., Perry, J.J. (2011). Determination of quaternary ammonium compounds in seawater samples by solid-phase extraction and liquid chromatography –mass spectrometry. *Journal of Chromatography A*, 1218, 673-677, doi:10.1016/j.chroma.2010-11.088

Bonilla Simon, M. M., Cozar, A.E., Diez, M.P. (1990). Spectrophotometric determination of cationic surfactants in frozen and fresh squid by ion-pair formation with methyl orange. *Analyst*, 115, 337-339.

Brunauer, S.; Emmett, P. H.; Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*. 60 (2), 309–319. ISSN 0002-7863. doi:10.1021/ja01269a023.

El-Khateeb, S. and Abdel-Moety, E.M.. Determination of quaternary ammonium surfactants in pharmaceutical formulations by the hypochromic effect. *Talanta*, Volume 35, Issue 10, October 1988, 813-815

Federle, T.W., Itrich, N.R. (1997). Comprehensive approach for assessing the kinetics of primary and ultimate biodegradation of chemicals in activated sludge: application to LAS. *Environ Sci Technol*. 31:1178-1184. doi: 10.1021/es9606891

Hellberga, P.E., Bergströma, K., Holmbergb, K. (2000). Cleavable Surfactants, *Journal of Surfactants and Detergents*, Vol. 3, No. 1, 81-91

Kester, D. R., Duedall, I. W., Connors, D. N., Pytkowicz, R. M. (1967*). Preparation of Artificial Seawater*. Limnology

Kronberg, B., Holmberg, K.,Lindman, B. (2017). *Surface Chemistry of Surfactants and Polymers*.Wiley: Pro-ed.Internet Document

Kruk. M and Jaroniec M. (2001).Gas Adsorption Characterization of Ordered Organic−Inorganic Nanocomposite Materials. *Chem. Mater*., 13 (10), 3169–3183. DOI: 10.1021/cm0101069

Motomizu, S., Oshima, M., Hosoi, Y. (1992). Spectrophotometric determination of cationic and anionic surfactants with anionic dyes in the presence of nonionic surfactants. Part I: General aspect, *Mikrochim. Acta*, 706, 57-66

Overkempe, C., Annerling, A., Gingel, C., Tomas, P.C., Boltersdort, D., Speelman, J. (2005). *Novel Surfactants: Preparation, Application and Biodegradability. Esterquats.* Marcel Dekker A G. N. Basel.

Para, G., Łuczyński, J., Palus, J., Jarek, E., Wilk, K.A., Warszyński, P.(2015). Hydrolysis driven surface activity of esterquats surfactants. *Jour.Colloid.Inter Sc*., 465, 174-182. doi: 10.1016/j.jcis.2015.11.056

Roy, S., Baer, M.D., Mundy, C.J., Schenter, G.K. (2017). Marcus Theory of Ion-Pairing. *J. Chem. Theory Comput.* 13, 3470−3477

Rubingh, D.N., Holland, P.M. (1992).*Cationic Surfactants: Physical Chemistry, Surfactant Science Series*, 37, MarcellDekker,NY, 449

Schmitt, T.M. (2001). *Analysis of surfactants*. BASF corporation. W.Michigan,published by Marcel Dekkert,Inc,NY.Basel,2001,637

Swisher, R.D. (1987*) Surfactant Biodegradation*. 2nd Edition, revised and expanded. Surfactant science series, Volume 18, Marcel Dekker, New York and Basel

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. (2003). Environmental Organic Chemistry. Wiley Interscience 2nd ed

Waters, J., W. Kupfer, (1976). Cationic surfactants in the presence of anionic surfactant in biodegradation test liquors, *Anal. Chim. Acta*, 85, 241-251

Wulf, V., Wienand, N., Wirtz, M., Kling, H.W., Gäb, S., Schmitz, O.J. (2010). Analysis of special surfactants by comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry. *Journal of Chromatography A*. 1217: 749–54. doi: 10.1016/j.chroma.2009.11.093

Yamamoto, K., Motomizu, S. (1991). Spectrophotometric method for the determination of ionic surfactants by flow injection analysis with acidic dyes, *Anal. Chim. Acta*, 246, 333-339.

Zhang, C., Cui, F., Zeng, G., Jiang, M., Yang, Z., Yu, Z., Zhu, M., Shen, L. (2015). Quaternary ammonium compounds (QACs): A review on occurrence, fate and toxicity in the environment. *Science of the Total Environment*.518-519, 352-362, http://dx.doi.org/10.1016/j.scitotenv.2015.03.007