Analysis of Interactions between Colloidal Wood Pitch and Various Mineral Particles by Flow Cytometry

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The interactions between colloidal wood pitch and various commercially available mineral particles were assessed. The experiments were conducted by adding PCC, GCC, kaolin, and bentonite particles to laboratory-made pitch emulsions, and the mixtures were analyzed using flow cytometry. The results showed that most of the tested minerals were quite hydrophilic. The hydrophobicity of the mineral particles increased significantly in the presence of colloidal pitch, which showed that interactions between the pitch and the mineral surfaces occurred. The charge of the mineral particles was very important; the pitch–mineral populations formed with cationic minerals were more hydrophobic than those formed with anionic minerals. Water-soluble galactoglucomannans from spruce diminished the adsorption of pitch onto cationic minerals, while they had no significant effect on the adsorption of pitch onto anionic minerals.

Keywords: Colloidal pitch; Galactoglucomannans; TMP; Pigments; Minerals; Filler; Additives; Interactions; Wood resin; Flow cytometry; Deposits

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INTRODUCTION

A wide variety of wood components are released from Norway spruce (*Picea abies*) during production of thermomechanical pulp (TMP) and in the subsequent papermaking process (Örså *et al.* 1997). These components are commonly called dissolved and colloidal substances (DCS). The DCS consist of water-soluble hemicelluloses, lipophilic and hydrophilic extractives, lignin fragments, and inorganic salts. The lipophilic extractives are commonly referred to as ‘pitch’ in papermaking. The pitch in TMP can be smeared onto fiber surfaces, located inside unbroken parenchyma cells, and dispersed in the process water as colloidal droplets (Allen 1975). About 80% of the pitch is normally found in colloidal form. The colloidal pitch is the most troublesome in papermaking, as uncontrolled aggregation of colloidal pitch can lead to problems, such as formation of deposits on various paper machine surfaces, spots and holes in the paper, and overall problems with runnability (Allen 2000).

The colloidal pitch consists of two parts: the most hydrophobic pitch components, *i.e.*, triglycerides and steryl esters, are found in the core of the droplets, while resin and fatty acids are located on the surface of these droplets (Qin *et al.* 2003). The pH-dependent anionic charge of the colloidal pitch droplets is a result of dissociated carboxyl groups of resin and fatty acids.

Several methods have been developed to try to minimize the impact of pitch on the papermaking process, such as deresination of pulps prior to papermaking, removal of the pitch by flotation (Back 2000; Tanase-Opedal *et al.* 2011; Strand *et al.* 2012), binding of the pitch to the formed paper by polyelectrolytes, adsorbing the pitch onto inorganic particles, or dispersing the pitch to avoid uncontrolled aggregation (Allen 2000).

Water-soluble galactoglucomannans (GGM) are dissolved from Norway spruce during pulping. GGM have been shown to stabilize colloidal wood pitch sterically against aggregation by simple electrolytes (Sundberg *et al.* 1996b; Hannuksela and Holmbom 2004). The presence of solids, such as TMP fibers, diminishes the steric stabilization of colloidal pitch by GGM against aggregation by calcium ions (Strand *et al.* 2011).

Fillers, such as kaolin, bentonite, talc, ground calcium carbonate (GCC), and precipitated calcium carbonate (PCC), are currently widely used in papermaking applications. Kaolinites and bentonites are flake-like particles consisting of layered crystalline structures (van Olphen 1955; Solomon and Hawthorne 1983a). The flake-like particles are amphoteric because they develop cationic charges along their edges and anionic charges on their basal surfaces in neutral or weakly acidic media (Eklund and Lindström 1991). PCC is usually cationic under papermaking conditions, while GCC particles are anionic due to adsorption of anionic impurities or anionic dispersing aids used in production.

Interactions between wood pitch components and minerals have previously been studied by adsorption experiments with oleic acid, a fatty acid, and triolein, a triglyceride, onto various mineral surfaces (Rogan 1994). An extensive study was performed by adsorbing either oleic acid or triolein onto the minerals and fitting the results to available adsorption isotherms. It was found that the mineral surface type and surface treatment of the minerals both played a major role in adsorption.

Adsorption studies of oleic acid and abietic acid and DCS from peroxide-bleached TMP onto PCC and talc pigments have shown that PCC does adsorb both oleic and abietic acid (Miyanishi *et al.* 2000). PCC adsorbed ten times more fatty acid than resin acid. Anionic DCS substances were adsorbed onto the PCC until the cationic charge of the PCC was neutralized.

Interactions between different minerals and DCS from spruce have also been studied by mixing peroxide-bleached or unbleached TMP water with mineral particles (Willför *et al.* 2000). The mixture was then centrifuged, and the DCS components in the supernatant were analyzed by gas chromatography and total organic carbon determinations. It was seen that additions of kaolin removed some pitch, GGM, and pectins from unbleached and peroxide-bleached TMP water at pH 5 and 8. The adsorption to PCC at pH 8 was more selective because the PCC adsorbed pitch, and significantly less GGM were removed compared with the result when kaolin was added. The TMP water used in the study contained fines, hemicelluloses, hydrophilic extractives, and lipophilic extractives. It was therefore difficult to draw clear conclusions about the interactions between mineral surfaces and pitch due to the wide range of other wood components present in the system.

Adsorption experiments with DCS onto talc, magnesium aluminum silicate, and kaolin particles have also been reported (Mosbye *et al.* 2003). The adsorption of colloidal pitch was determined by turbidity measurements of the samples after centrifugation. It was seen that more pitch was removed when more mineral particles were added, independent of which filler was added. It was also seen that less pitch was removed when dissolved substances from spruce were added, compared with when no dissolved substances were added.

Adsorption experiments with unbleached DCS onto GCC, surface-modified GCC, and talc have been reported (Gantenbein *et al.* 2012). It was seen that very high concentrations of native GCC were needed in order to achieve significant pitch removal, while much lower concentration was needed of the surface-modified GCC.

These previous studies have mostly focused on the adsorption of pitch onto minerals, by determinations of the pitch concentration before and after the addition of mineral particles (Rogan 1994; Willför *et al.* 2000; Mosbye *et al.* 2003; Gantenbein *et al.* 2012). Centrifugation has been used to separate the minerals from the pitch, and the remaining pitch in the supernatant has been determined by HPLC, GC, turbidity measurements, or TOC. Centrifugation of a colloidal pitch emulsion in the presence of salts caused some destabilization of otherwise stable colloids, which was also seen by Rogan (1994). Filtration of the samples may also lead to misleading results, due to the low solubility of calcium soaps of fatty acids in water (MacNeil *et al.* 2011). A method to study the interactions between colloidal wood pitch and mineral surfaces that does not require centrifugation or filtration could therefore be preferable.

The properties of the mineral surfaces after pitch adsorption, however, have not been mentioned at all. The hydrophobicity of the mineral surfaces after the adsorption of pitch should be of great interest for papermakers because these are the surfaces that they either have to attach to fiber surfaces or to disperse to avoid deposition in the paper machine. Understanding the interactions between colloidal wood pitch and mineral particles in process waters is of utmost importance to ensure good runnability and to avoid troublesome deposits (Winters 1998). Deposits found in pulping and papermaking usually consist of mixtures of organic and inorganic components (Sitholé 2000). The deposition tendency of pitch is usually quite complex and highly dependent on the variables in the system (Dreisbach and Michalopoulos 1989).

Reflectometry has for instance been used to study the adsorption of unbleached and peroxide-bleached DCS and pitch on SiO_2 and Al_2O_3 surfaces (Kekkonen and Stenius 1999). It was noted, however, that the complexity of the DCS composition caused some difficulties in the interpretation of the results with this method.

Flow cytometry (FCM) is a new method adapted to the field of papermaking and pulping. FCM analysis is a very efficient way to study interactions between particles such as colloidal pitch droplets or bacteria in papermaking process water (Vähäsalo *et al.* 2003; Lindberg *et al.* 2004; Vähäsalo and Holmbom 2005). FCM analysis is very rapid, and it is possible to get almost on-line feedback from the process regarding information that otherwise would be difficult to obtain. FCM has recently been used to study the adsorption of pitch in debarking water using kaolin and talc (Leiviskä *et al.* 2012). Depending on the kaolin quality, pitch removal by adsorption onto kaolin was found to be almost as effective as adsorption onto talc.

The aim of this study was to determine the interactions between colloidal wood pitch and a few commonly used mineral particles in water in a systematic and qualitative way by the use of flow cytometry. The aim was also to determine if and how the presence of water-soluble galactoglucomannans influences the interactions between colloidal pitch and mineral particles.

EXPERIMENTAL

Materials and Methods

Pitch emulsion

TMP from Norway spruce was freeze-dried and Soxhlet-extracted using hexane. The extract was evaporated and re-dissolved in acetone to a concentration of 30 g/L. Pitch emulsions were prepared by injecting the dissolved extractives in acetone into distilled water during agitation and subsequent dialysis (cut-off 12 to 14 kDa, Medicell International, UK) according to the method described by Sundberg *et al.* (1996c). The concentration of pitch in the emulsions after dialysis was 360 to 390 mg/L, determined by gas chromatography (Örså and Holmbom 1994). The pitch was composed of about 6% fatty acids, 27% resin acids, 16% steryl esters, 43% triglycerides, and 6% other components. Laboratory-made pitch emulsions were used in this study to avoid fines, which are present when using DCS water from TMP or real process water. The presence of fines would have made the interpretation of the flow cytometry data much more difficult.

Galactoglucomannans

Galactoglucomannans (GGM) were isolated at a Finnish paper mill using Norway spruce by ultrafiltration and subsequent spray-drying (Xu *et al.* 2007). A stock solution of GGM was prepared by dissolving them directly in distilled water to a concentration of about 5.8 g/L, as determined by gas chromatography after methanolysis (Sundberg *et al.* 1996a).

Mineral particles

Prismatic precipitated calcium carbonate (PCC), Albaglos S, was received from Specialty Minerals, New York, USA. The prismatic PCC was received as slurry, with a dry content of 70.6%. The particle size distribution (PSD) was reported as PSD 20% 0.46 µm, PSD 50% 0.64 µm, and PSD 90% 1.07 µm. The 325-mesh residue was 0.001%. The prismatic PCC was diluted with pH-adjusted distilled water (pH 8) to a consistency of 5.3%.

Scalenohedral PCC, Velacarb, was received from Specialty Minerals Nordic, Anjalankoski, Finland. The scalenohedral PCC was received as slurry, with a dry content of 13.8%. The PSD was reported as PSD 20% 0.69 µm, PSD 50% 1.29 µm, and PSD 90% 2.37 µm. The 325-mesh residue was 0.0009%. The scalenohedral PCC slurry was used as received.

The ground calcium carbonate (GCC) used in the experiments was a commercially available GCC, which was received as slurry, with a dry content of 71.3%. The particle size distribution (PSD) was reported as PSD 20% 1.36 µm, PSD 50% 1.53 µm, and PSD 90% 2.19 µm. The GCC slurry was diluted with distilled water to a consistency of 5.4%.

Kaolin, Intramax JR, was received from Imerys Minerals, Par Cornwall, UK. The kaolin was received in powder form, with a moisture content of 18%. It was reported that 24 mass% of the particles had a diameter below 1 µm, and 38 mass% had a diameter below 2 µm. The 325-mesh residue was 0 ppm. The kaolin was dispersed in distilled water to a consistency of 5.9%.

Three different bentonite samples, Pitchbent K, Pitchbent UF, and EXM 1694, were received from Clariant Produkte (Deutschland), Moosburg, Germany. The bentonites were received in powder form and dispersed in distilled water to a consistency of 5.2 to 5.5%. An overview of the abbreviations used for the different mineral particles is found in Table 1. The minerals chosen for this study were meant to represent typical minerals that colloidal wood pitch may encounter in a papermaking process water using TMP. These minerals are either used as fillers or additives for pitch adsorption.

Table 1. Mineral Particles Used in the Experiments

Term	Product Name	Type of Additive
PCC A	Albaglos S	Prismatic PCC
PCC B	Velacarb	Scalenohedral PCC
GCC	-	GCC
Kaolin	Intramax JR	Kaolin
Bentonite A	Pitchbent K	Modified bentonite
Bentonite B	Pitchbent UF	Bentonite
Bentonite C	EXM 1694	Special bentonite

Determination of particle charge

The charge of the mineral particles was determined by polyelectrolyte titration with 1,5-dimethyl-1,5-diazaundecamethylene polymethobromide (polybrene, 8×10^3 Da, Sigma) and potassium polyvinyl sulfate (KPVS) through back-titration using a particle charge detector (Mütek PCD 03), also known as a streaming current detector (Holmbom *et al.* 2000).

Different doses of polybrene or KPVS were added to suspensions of the mineral particles. The suspensions were stirred for 1 h to ensure sufficient opportunity for polymer adsorption. After 1 h, the suspensions were filtered through syringe filters with a pore size of 0.2 (Titan 3, nylon membrane, Purple) or 0.1 µm (Whatman International, inorganic membrane filter, Anotop 25 Plus), depending on the reported size of the particles. The filtrates, as well as blank samples, were titrated with KPVS or polybrene in the particle charge detector to determine the concentration of unadsorbed polybrene or KPVS. The determined concentrations from the measurements were used to plot adsorption isotherms, from which the charge of the mineral particles was extrapolated (Table 2).

From the obtained charge values it was seen that PCC A and the GCC contained anionic dispersing agents, which rendered the net charge of these particles anionic. The dispersing agents are needed in order to produce slurries with high dry content.

Table 2. The Determined Charge of the Mineral Particles

Term	Charge, µeq/g	Type of Charge
PCC A	−72 (pH 7)	Anionic
PCC B	+39 (pH 9)	Cationic
GCC	−44 (pH 7)	Anionic
Kaolin	−100 (pH 5)	Anionic
Bentonite A	−1800 (pH 7)	Anionic
Bentonite B	−2100 (pH 7)	Anionic
Bentonite C	−850 (pH 6)	Anionic

Experimental setup

First, 25 mL of pitch emulsion was measured into a bottle. Different volumes of GGM stock solution were added to the pitch emulsion, and the mixture was diluted to 50 mL with filtered distilled water. The starting concentration of colloidal pitch in the experiments was 186 mg/L, with a relative standard deviation of about 4%. The mixture was agitated using a magnetic stirrer throughout the experiment. Small doses of mineral slurry, *i.e.*, PCC, GCC, kaolin, or bentonite in water, were added to the mixture and allowed to react for about 5 min. A small sample was then pipetted from the mixture for analysis by flow cytometry.

Flow cytometry

Flow cytometry (FCM) was performed with a Partec CyFlow Blue apparatus. The light scattered by the particles was recorded as forward scattering (FSC) and as side scattering (SSC, 90°). The cytometer was equipped with three different fluorescence channels: FL1 (512 to 542 nm, green), FL2 (575 to 605 nm, orange) and FL3 (615 to 645 nm, red). Filtered distilled water was used as a sheath fluid in the analysis. Nile red (Tamro, Vantaa, Finland) was used as a fluorescent dye to stain the lipophilic components in the samples, similar to previously published studies (Vähäsalo *et al.* 2003; Vähäsalo and Holmbom 2005).

The experimental samples were diluted 20 to 200 times with filtered distilled water prior to analysis, depending on the amount of particles in the sample. A methanol solution of Nile red (10 ppm) was used to stain the lipophilic substances. The red fluorescence intensity (FL3) was used as an indicator of the amount of lipophilic material on the particle surfaces. The populations were gated using Partec FloMax software (v. 2.4f), which made it possible to calculate the mean hydrophobicity of the different particle populations (Vähäsalo *et al.* 2003).

RESULTS AND DISCUSSION

Samples containing only colloidal wood pitch, kaolin, GCC, PCC, or bentonite were analyzed by FCM. The light scattering in the forward direction (FSC) of the particles was plotted against the intensity of fluorescence in the FL3 range of the particles (Fig. 1). FSC is an indirect measurement of particle size and is also influenced by the refractive index of the particles. The intensity of light in the FL3 region is a measurement of the hydrophobicity of the particle surface. Nile red is an environment-sensitive fluorophore; it is almost non-fluorescent in hydrophilic environments, while it undergoes a fluorescence enhancement and large absorption and emission blue shifts in hydrophobic environments. However, the FL3 values are also influenced by particle size in that larger particles are able to bind to more hydrophobic material and therefore emit more fluorescence from Nile red.

Colloidal wood pitch is known to be quite hydrophobic because it consists of lipophilic extractives from wood. The most hydrophobic pitch components, *i.e.*, triglycerides and steryl esters, are shielded from the surrounding water by a surface layer of resin and fatty acids, but the nature of a pitch droplet is still quite hydrophobic. The FL3 values for colloidal wood pitch stretched from about 0.5 to 100, with a mean value of about 9 (Fig. 1a). The position of the pitch population on the x-axis implied that particles with FL3 > 2 could be considered hydrophobic.

The FL3 mean value for kaolin and GCC particles was about 0.2 (Fig. 1b, c), indicating that very little Nile red was adsorbed onto these mineral surfaces and that the mineral particles therefore were quite hydrophilic. It is known that charged mineral surfaces have a tendency to form hydrogen bonds with the surrounding water (Solomon and Hawthorne 1983b). Most aluminosilicate minerals have highly polar surfaces that are hydrophilic. The hydrophobicity of the kaolin particle population was lower in this study compared with the previously published hydrophobicity of kaolin, as determined by FCM (Leiviskä *et al.* 2012). The low hydrophobicity of the kaolin particles implied that the amount of adsorbed contaminants was much lower in this study compared with previously published results.

PCC A and PCC B particles (Fig. 1d, e) gave similar FL3 values as kaolin and GCC pigments. Most of the bentonite A and B particles had FL3 values below 0.1 (Fig. 1f, g) and were extremely hydrophilic. The flow cytometer used was set up in such a way that the lower limit of detection of particles was around 0.1 µm, and the lower limit for FL3 was 0.1.

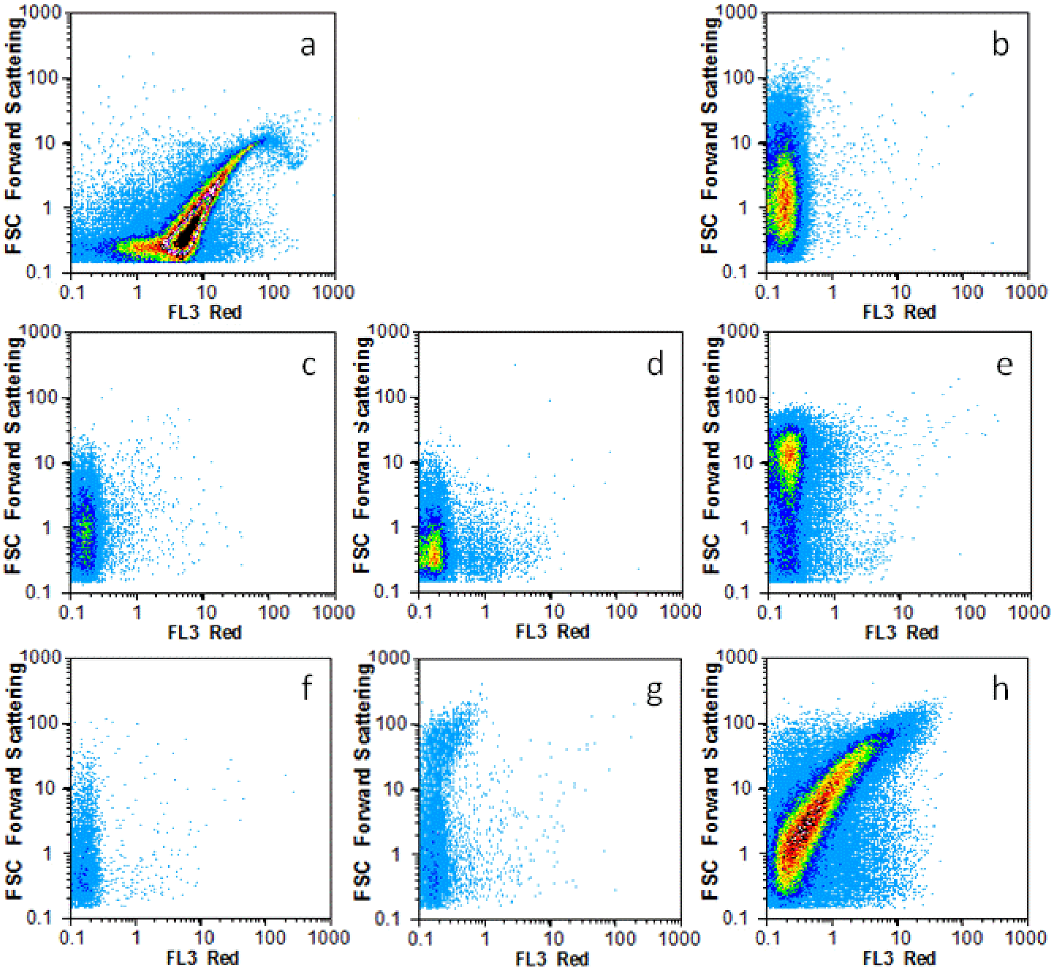

Fig. 1. Logarithmic plots of light scattering in the forward direction (FSC) versus the intensity of fluorescence in the FL3 region (hydrophobicity) of various particles: a) Colloidal wood pitch with a concentration of 190 ppm; b) Kaolin–590 ppm; c) GCC–530 ppm; d) PCC A (prismatic)–530 ppm; e) PCC B (scalenohedral)–530 ppm; f) Bentonite A–530 ppm; g) Bentonite B–550 ppm; h) Bentonite C–520 ppm

Particles that were smaller than 0.1 µm and that emitted less light in the FL3 region than 0.1 were therefore not visible in the measurements. Bentonite C had FL3 values ranging from 0.1 to 10 (Fig. 1h), which showed that some of the particles were much more hydrophobic than bentonite A and B. The bentonite samples showed that large variations are possible between similar products. These preliminary FCM analyses showed that all the tested mineral pigments were quite hydrophilic in the absence of hydrophobic substances. Bentonite C, which contained particles that could be considered hydrophobic, was the only exception.

Wood Pitch with Kaolin

Addition of 120 ppm kaolin to the pitch emulsion resulted in a new population, as determined by FCM (Fig. 2). The newly formed population had a mean FL3 value of 1.9, which indicated that their surfaces were slightly less hydrophobic than colloidal pitch, but more hydrophobic than kaolin (Fig. 1a, b). The new population was a result of the interaction between colloidal pitch and kaolin particles. It seemed that the kaolin particles were not completely covered by pitch, as they were less hydrophobic than colloidal pitch. Most likely, pitch adsorption onto the cationically charged edges of the kaolin particles was favorable, while less pitch would adsorb on to the anionic surfaces of the kaolin.

Increasing the kaolin amount to 590 ppm resulted in a broader distribution of kaolin–pitch particles (Fig. 2), but the mean FL3 value of the population was 2.1, *i.e.*, similar to the one at 120 ppm kaolin. The broad distribution of kaolin–pitch particles along the FL3 axis indicated that the kaolin still adsorbed available pitch, but also that some of the kaolin particles adsorbed less pitch. This could be due to the fact that some of the kaolin particles had a smaller surface area than others, and therefore were able to adsorb less pitch.

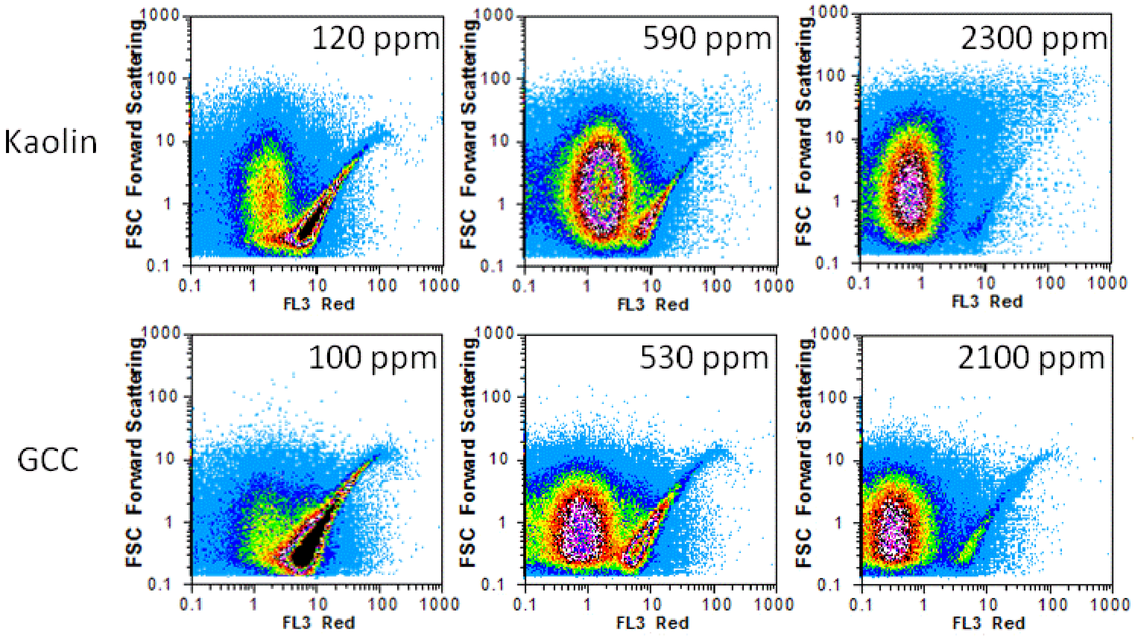

Fig. 2. Light scattering versus hydrophobicity of colloidal pitch droplets with kaolin and GCC particles, plotted in logarithmic scale

Deposition experiments with DCS on oxide surfaces have previously determined that pitch does not deposit onto surface layers of deposited DCS, *i.e.*, a clean oxide surface is needed for adsorption of pitch (Kekkonen and Stenius 1999). This could be an explanation for why the kaolin only adsorbs a certain amount of pitch and why the pitch does not continue to accumulate on top of the adsorbed pitch.

Increasing the amount of kaolin further to 2300 ppm lowered the mean FL3 value of the kaolin–pitch particles to 1.1. The mean hydrophobicity of the pitch–kaolin particles decreased due to the decreased concentration of colloidal pitch in combination with additional hydrophilic kaolin surfaces being introduced to the mixture. The pitch–kaolin particles at 2300 ppm were still significantly more hydrophobic compared with clean kaolin particles; the colloidal wood pitch had a permanent influence on the total hydrophobicity of the kaolin population, even though the pitch itself was depleted at some point. The hydrophobicity in the kaolin–pitch population in these measurements was quite similar to previously published results (Leiviskä *et al.* 2012), *i.e.*, the hydrophobicity was significantly higher than for pure kaolin in distilled water.

Wood Pitch with GCC

The FCM results when adding GCC to pitch emulsions were quite similar to the kaolin experiments, with formation of a pitch–GCC particle population that was slightly less hydrophobic than colloidal pitch (Fig. 2). The pitch–GCC population could, however, not be distinguished from the pitch population at 100 ppm GCC. The mean hydrophobicity of the population decreased with increasing amounts of GCC, as in the experiments performed with kaolin. The pitch–GCC population at 2100 ppm had a low FL3 mean value of 0.7, but was still more hydrophobic than GCC in the absence of pitch. These results indicated that neither kaolin particles nor GCC particles were completely covered by wood pitch due to the fact that their surface hydrophobicity was lower than the surface hydrophobicity of colloidal wood pitch.

Wood Pitch with PCC

Two different types of PCC particles were added to wood pitch emulsions. Additions of PCC A (prismatic PCC) (Fig. 3) gave results that were very similar to the experiments performed with kaolin and GCC particles (Fig. 2). Adsorption of pitch onto the PCC A particles resulted in a population of pitch–PCC A particles that had an FL3 value slightly lower than that of colloidal pitch. The surfaces of PCC A were not completely covered by the pitch because the surface hydrophobicity of these particles was lower than that of colloidal pitch. Increasing the amount of PCC A shifted the mean FL3 value of the population toward lower values, from 1.2 at 530 ppm to 0.6 at 3000 ppm, much like in the experiments with kaolin and GCC.

Additions of PCC B (scalenohedral PCC) to the pitch emulsion resulted in a population of pitch–PCC B particles with a higher FL3 value than colloidal pitch (Fig. 3). The formed population with 530 ppm of PCC B had a mean FL3 value of 43. The hydrophobicity of the pitch-PCC B population was most likely similar to that of colloidal pitch, but appeared more hydrophobic due to the large size of the formed aggregates. Increasing the concentration of PCC B from 530 to 2000 ppm further increased the surface hydrophobicity of the PCC B–pitch population while depleting the original pitch population.

Increasing the concentration of PCC B even further, to 3000 ppm, showed that more particles were formed in the FL3 range of 0.3 to 1, *i.e.*, the particles were much less hydrophobic than the first pitch–PCC B population (Fig. 3). The PCC added after this point was not covered by hydrophobic substances because the added PCC had previously adsorbed all of the available pitch at 3000 ppm.

PCC A and B both consist of calcium carbonate, but PCC A was anionic, while PCC B was cationic (Table 2). Repulsion between the anionic charges on the colloidal pitch and the anionic charges on PCC A meant that collisions leading to adsorption were quite infrequent and that the formed pitch–PCC A population was less hydrophobic than the pitch by itself. The cationic scalenohedral PCC was much more susceptible to pitch adsorption than the anionic prismatic PCC A. Attraction between the anionic charges of the colloidal pitch and the cationic charges of PCC B led to a high rate of adsorption. The pitch most likely accumulated within the scalenohedral structure and seemed to completely cover the surface of PCC B.

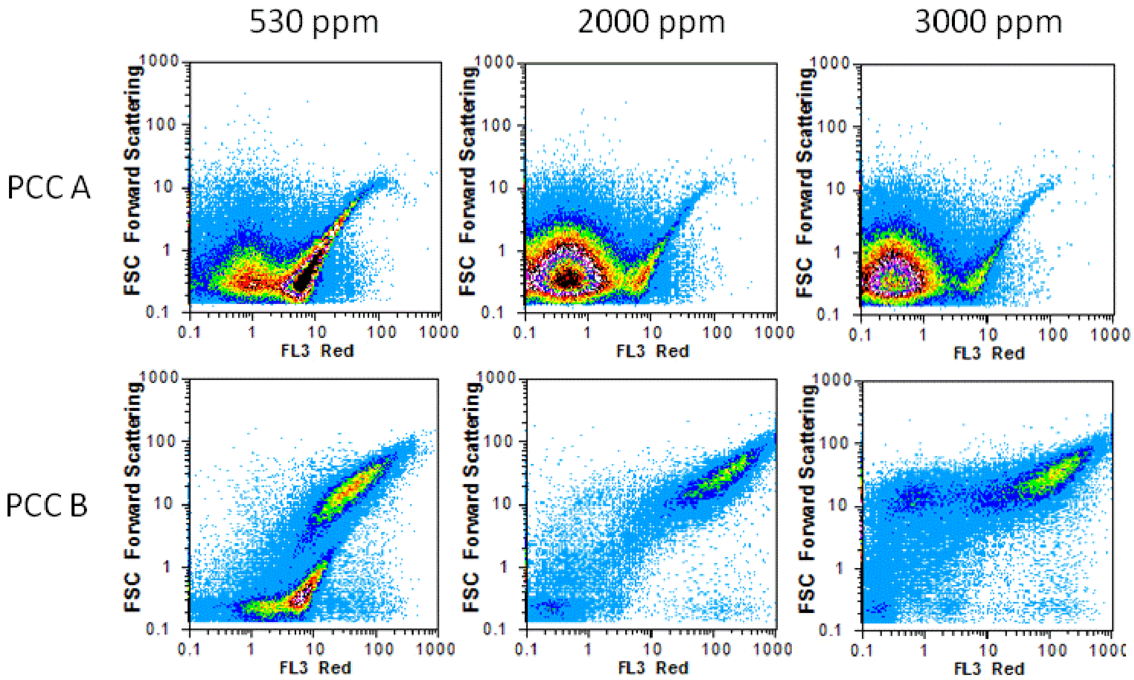

Fig. 3. Light scattering versus hydrophobicity of colloidal pitch droplets and different PCC particles, plotted in logarithmic scale

Wood Pitch with Bentonite

Addition of 500 ppm of the different bentonites to the pitch emulsion resulted in new pitch–bentonite populations, as demonstrated by FCM (Fig. 4). The pitch–bentonite populations were slightly less hydrophobic than colloidal pitch. The bentonite particles were not completely covered by pitch. Bentonite, like kaolin, has a flake-like structure with anionic surfaces and cationic edges. The cationic edges were probably also in this case the most active part in adsorbing pitch. It has been reported that also the internal surface of bentonites also may be active in pitch-adsorption, due to swelling of the bentonite structure in water (Asselman and Garnier 2000).

Increasing the concentration of the bentonites to 1000 ppm caused the pitch–bentonite populations to shift toward lower FL3 values (Fig. 4). The remaining colloidal pitch population at 1000 ppm of bentonite B and C had a slightly lower FL3 value than with bentonite A. It seemed that some of the bentonite B and C got adsorbed onto the colloidal pitch droplets, effectively lowering the surface hydrophobicity of the remaining pitch population. This change in pitch hydrophobicity was unique for bentonite B and C; none of the other minerals tested showed this type of behavior.

Increasing the concentration of bentonite to 3000 ppm further shifted the mean hydrophobicity of the pitch–bentonite particles toward lower FL3 values with bentonite B and C. This indicated that the available colloidal pitch had been almost depleted at an earlier stage. Bentonite A was still adsorbing pitch at 3000 ppm, which can be seen by the remaining pitch population in Fig. 4. According to these results, bentonite B and C were more efficient at adsorbing pitch than bentonite A.

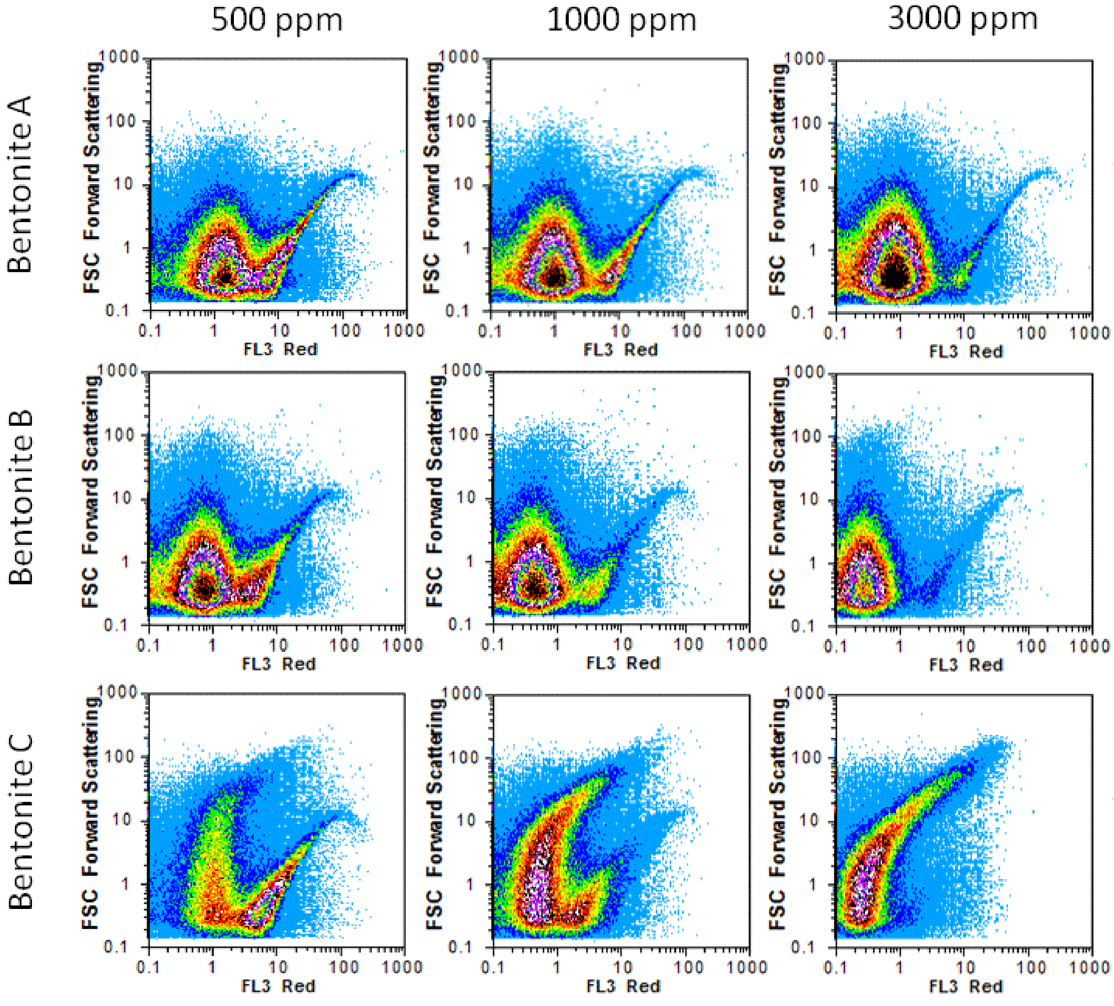

Fig. 4. Light scattering versus hydrophobicity of colloidal pitch droplets with different bentonite particles, plotted in logarithmic scale

The interaction between colloidal wood pitch and mineral surfaces is a complex system because the pitch droplets consist of a mixture of resin acids, fatty acids, steryl esters, and triglycerides. Rogan (1994) showed that montmorillonite adsorbed oleic acid quite effectively, while much less triolein was adsorbed. Miyanishi *et al.* (2000) showed that PCC adsorbed both oleic and abietic acid, and also that about ten times more oleic acid than abietic acid was adsorbed. The cationic charge of the PCC particles was most likely neutralized by the anionic fatty or resin acids, which caused aggregation of PCC particles. The anionic charges of colloidal pitch seemed to be attracted by the cationic charges on the mineral surfaces, *e.g.*, the cationic edges of kaolin plates.

The large difference in hydrophobicity between the pitch populations formed with anionic mineral particles and the cationic PCC B (scalenohedral) populations showed that the type of charge of the mineral particle is extremely important for determining both the attraction and repulsion between mineral particles and colloidal pitch and the hydrophobicity of the formed mineral–pitch populations.

Wood Pitch with GGM

It is known that galactoglucomannans (GGM) from spruce stabilize colloidal pitch droplets sterically against aggregation by metal ions (Sundberg *et al.* 1996b). Colloidal wood pitch has also been shown to cause fewer problems with deposits in the presence of GGM. Pitch emulsions were mixed with different aliquots of GGM solution, to GGM concentrations of 0, 580, and 2900 ppm. FCM analysis of the emulsions showed that the hydrophobicity, shape, and position of the pitch populations were quite similar with 0, 580, and 2900 ppm GGM (Fig. 5). However, the measured mean hydrophobicity of the colloidal pitch droplets decreased slightly with the added GGM: to 9.8 at 0 ppm GGM, 9.1 at 580 ppm GGM, and 7.8 at 2900 ppm GGM.

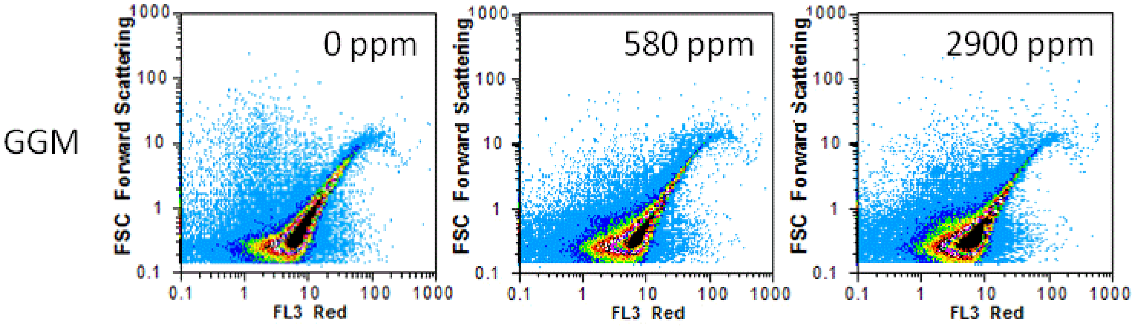

Fig. 5. Light scattering versus hydrophobicity of colloidal pitch droplets with GGM concentrations of 0, 580, and 2900 ppm, plotted in logarithmic scale

Experiments were performed by adding PCC B (scalenohedral PCC) to wood pitch emulsions with varying concentrations of GGM, and the interactions between the particles were studied using FCM (Fig. 6). As stated earlier, the formed pitch–PCC population with PCC B was very hydrophobic because the pitch completely covered the PCC in the absence of GGM. Particles in the FL3 range of 0.3 to 1 started forming at 3000 ppm PCC and increased to a quite significant population at 4800 ppm PCC.

A very low GGM concentration, only 30 ppm, already had a noticeable effect on the interactions between the pitch and the PCC. The mean FL3 value of the pitch–PCC population with 30 ppm GGM was 1,2 compared with 43 when no GGM was added at 530 ppm of PCC; *i.e.*, the pitch–PCC particles were less hydrophobic when GGM was added.

Further increasing the PCC concentration to 3000 ppm resulted in a very broad distribution along the FL3 axis with 30 ppm GGM. The low concentration of GGM could only lower the hydrophobicity of the pitch–PCC particles at the initial PCC addition, while very hydrophobic aggregates were still formed when the PCC concentration was increased to 3000 ppm. Another effect of the GGM was that hydrophilic PCC started to form at a much higher PCC concentration, 4800 ppm, compared with the case when no GGM was added.

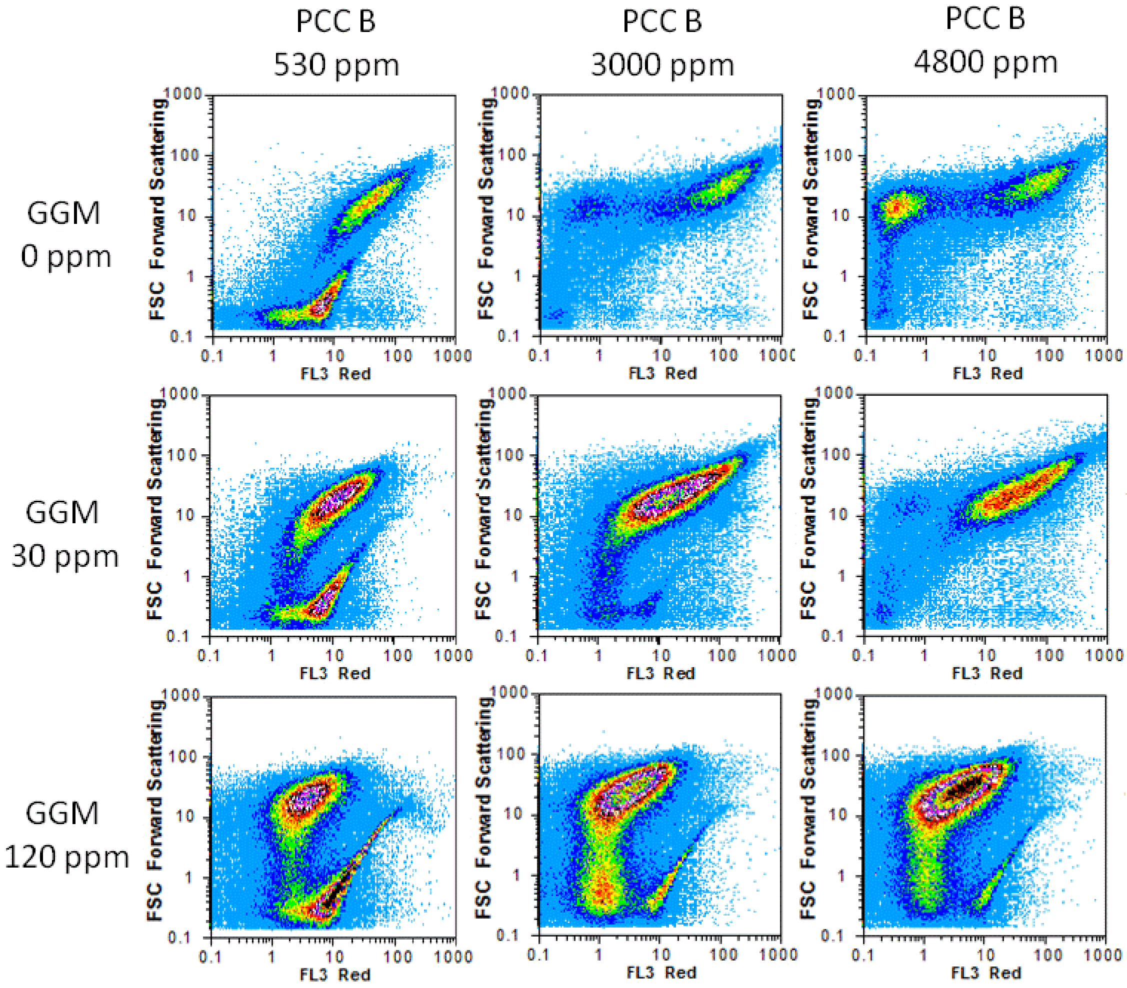

Fig. 6. Light scattering versus hydrophobicity of colloidal pitch droplets and PCC B (scalenohedral) particles, with 0, 30, and 120 ppm GGM, plotted in logarithmic scale

The effect of GGM on the interactions between pitch and PCC B was seen more clearly when the GGM concentration was increased to 120 ppm. The mean value of the pitch–PCC population at 530 ppm PCC with 120 ppm GGM was 5.2, compared with 43 when no GGM was added. With 120 ppm GGM, the mean FL3 value of the pitch–PCC population at 4800 ppm was only 4.9. Increasing the concentration of GGM further, to as high as 580 ppm, resulted in less hydrophobic pitch–PCC populations; *e.g.*, 1.9 with 580 ppm GGM at 3000 ppm PCC (no figure).

The added GGM somewhat diminished the adsorption of colloidal wood pitch onto PCC, as the formed pitch–PCC populations were initially less hydrophobic than was the case when no GGM was added. Low GGM concentrations could only diminish the adsorption of pitch at low PCC additions, while higher GGM concentrations were able to diminish the adsorption also at high PCC additions. It has been previously stated that PCC does not adsorb GGM (Willför *et al.* 2000), so the steric stabilization of the pitch was not hindered on the PCC surfaces. Similar behaviour has also been reported when using cationic GCC (Gantenbein *et al.* 2012). None of the tested GGM concentrations could completely prevent the pitch from adsorbing onto the scalenohedral PCC to some degree, *i.e.*, in the presence of colloidal pitch, the PCC was always more hydrophobic than pure PCC.

Experiments were also performed by adding kaolin to wood pitch emulsions with varying concentrations of GGM, and the interactions between the particles were studied by FCM. The formed pitch–kaolin populations had very similar FL3 values with 0 and 580 ppm GGM (Fig. 7); hence, the GGM had no significant effect on the interactions between pitch and kaolin. It has previously been shown that kaolin can remove some carbohydrates, mostly GGM, from unbleached TMP water (Willför *et al.* 2000). It has also been stated that GGM has an affinity for kaolin particles, as some kaolin particles no longer sediment with centrifugation after the addition of dissolved substances from spruce (Mosbye *et al.* 2003). However, any clear sign of interactions between kaolin and GGM, in the presence of colloidal pitch, was not seen in the FCM analysis.

Experiments were also performed by adding bentonite A to pitch emulsions with 0 and 580 ppm GGM (no figure). These experiments showed that the GGM had no significant effect on the interactions between bentonite A and pitch, much like in the experiments with kaolin. It was therefore concluded that the interactions between anionic mineral particles and colloidal wood pitch were unaffected by the presence of GGM.

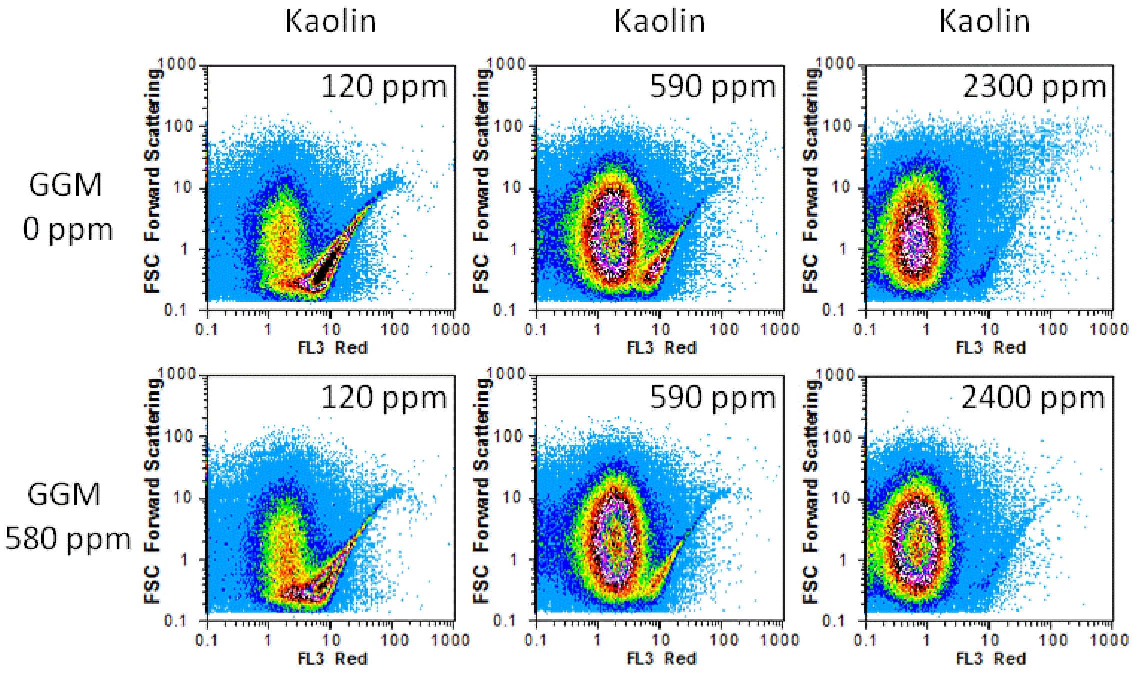

Fig. 7. Light scattering versus hydrophobicity of colloidal pitch droplets and kaolin particles with 0 and 580 ppm GGM, plotted in logarithmic scale

CONCLUSIONS

1. Most of the tested mineral particles are quite hydrophilic on their own. Measureable interactions between colloidal wood pitch and all of the tested minerals occurred. Anionic minerals form pitch–mineral populations that are less hydrophobic than colloidal wood pitch droplets. Cationic minerals may form pitch–mineral populations that are very hydrophobic. The hydrophobic aggregates formed with cationic minerals and colloidal pitch may cause deposits.
2. Water-soluble galactoglucomannans from spruce lowered the measureable hydrophobicity of colloidal pitch only slightly, as determined by flow cytometry. Addition of galactoglucomannans diminished the adsorption of pitch onto cationic scalenohedral PCC but had no significant effect on the interactions between pitch and anionic mineral surfaces such as kaolin and bentonite. Interactions between mineral particles and colloidal pitch cannot be completely prevented by galactoglucomannans. These results further support the conclusion that a high concentration of water-soluble galactoglucomannans in process water is essential for avoiding pitch problems in papermaking.
3. Flow cytometry is a quick and useful tool for studying the interactions between colloidal wood pitch and minerals particles in water. The measured hydrophobicity of the pitch-mineral populations may be used to identify runnability problems before they happen.

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