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BASF NOVEL IRON ORE BINDER TECHNOLOGY: STUDY OF BENTONITE MODIFICATION*

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Abstract

In this study, we compare the influence of two water soluble polymer-based organic binders added to bentonite, to form a hybrid-binder system for Iron Ore Pelletization. The kinetics of the agglomeration process and resulting properties of green pellets were analyzed, and examined in detail through Scanning Electron Microscopy (SEM) and Confocal Laser Scanning Microscopy (CLSM) analytical techniques. It was encountered that the differences in the mechanical properties of the pellets produced by each binder system could potentially be explained by the ability of the polymer to interact with bentonite at a macromolecular level.

Keywords: Iron Ore Pelletization; Organic Binders; Bentonite modification.

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1 INTRODUCTION

The globally degrading quality of iron ore preclude the use of lump ore (as common in the past) and require an enrichment process, resulting in fine-grained iron containing minerals which must be agglomerated and thermally hardened to form “pellets” to be effectively used in ironmaking process [3]. Pellets are then transported to Blast Furnace or Direct Reduction operations where they are reacted with reducing gases and melted to produce iron; iron is further refined and shaped into the wide variety of steel-based industrial and consumer products in use today.

Iron ore agglomeration is a wet process, where particles are held together by the surface tension and capillary forces when wet, they will fall apart upon drying unless binders are present. Most widely used binder is bentonite clay (ideally Sodium Montmorillonite), which has the disadvantage of increasing pellet silica and alumina content, reducing the value of the product. As an alternative, Organic Binders currently being marketed have not been widely accepted as an effective replacement of Bentonite for a number of reasons. Mainly the mechanical properties and surface quality of pellets produced with organic binders tend to be lower and totally ineffective in highly saline applications (fluxed pellets) [1].

In recent studies [2,5], it has been demonstrated that certain chemical substances such as hydrophilic polymers can strongly interact with bentonite clays modifying its structure at both crystalline and macromolecular levels. The interaction of polymers with bentonite, allowing modification of the clay macroscopic properties, has been studied from many angles with a useful overview provided e.g. by [8]. Also, the presence of other chemicals can affect the mechanical properties of the pellets. A fundamental understanding of how the polymer-bentonite interaction influences the agglomeration process and resulting pellet mechanical properties, is useful information for developing novel binders for the Iron Ore Pelletization process.

In line with this thought, in the past years BASF has invested important research and development efforts to create a new chemistry that can improve significantly the performance of polymer-bentonite systems. In the present work, we compare two binders: a traditional HPAM copolymer versus the new polymeric product (based on novel chemistry) as copolymers in an Iron Ore pelletization experiment.

Furthermore, to provide an insight on the phenomena behind the different performance observed, a Bentonite clay slurry modified with these two polymers was made, simulating the conditions encountered during Iron Ore pelletization (moisture, water chemistry as metal ion content, pH, and temperature) and dried completely. The dried material was analyzed with SEM and CLSM techniques to study the different bentonite morphologies encountered and the degree of interaction between polymer and bentonite.

2 MATERIAL AND METHODS

Materials

A sample of magnetite ore containing 63,7 wt% Fe, 4,5 wt% silica and 0,14 wt% alumina as well as 9,7 wt% moisture was used in this work. The bentonite used presented the following composition: 1,2%Ca, 1,9%Na, 9,3%Al and 29%Si. Polymer samples used were Standard HPAM (Alcotac™ FE 16, conventional partially hydrolyzed polyacrylamide) and Alcotac™ CS (proprietary acrylic type ter-polymer with unique viscosity profile) both from BASF, Germany. A commercially available amine-reactive pyrylium dye (Chromeo™, Active Motif, USA) was used to label the polymer binder molecules for CSLM studies.

Pelletization

The magnetite ore having 9,7% moisture was blended with a powdered pre-mix of binder formulation i.e. Bentonite alone or Bentonite plus organic binder, using a mixer machine brand Eirich model EL1, for three minutes. The resultant intimate mixture was subjected to pelletization by using an inclined pelletizing disk of 60 cm diameter, rotating at a speed of 33 rpm. The produced pellets had a size between 9.4 to 13.4 mm. Dry pellets were produced after drying for 3 hours at 110°C. The strength of dry pellets was determined using a Chatillon digital strength gauge. A total of 25 pellets were pressed in uniaxial direction and the maximum compressive strength recorded when the pellets were crushed. The dosages of bentonite and organic binder were 0,72 wt% in the case of no organic binder addition and 0,33 wt% bentonite plus 220g/t organic binder in the two conditions using polymer binders.

Suspension Preparation

Suspensions of bentonite alone (7,4 wt%) and bentonite plus organic binder (3,6% bentonite plus 0,23% organic binder) in distilled water were prepared [4]. These suspensions are equivalent to the bentonite and organic binder concentration found in the actual pelletization experiments.

Scanning Electron Microscopy and Focus Ion Beam Cutting

The suspensions of bentonite and bentonite plus organic binder were dried for 48 hours in an oven at 75°C. The surface of the dried bentonite samples was investigated by using a FEI Strata 400 machine (SEM combined with FIB). Additionally, to study the porosity resulting of the compaction of bentonite after the drying process, the cross section of the particles was investigated by cutting selected particles with a focused ion beam. This technique allows to visualize the differences in porosity of the dried sample not visible by simply scanning of the surface. This process requires an additional coating step of the surface with a 12-30nm Pt protective layer. The coating and cutting process description is described elsewhere [6].

Confocal Laser Scanning Microscopy

The two polymer samples were tagged with an amine-reactive pyrylium dye, at a dosage of 200ppm regarding the polymer weight. The dye become fluorescent upon reacting with primary amines, which are part of the polymer molecule composition. Suspension samples bentonite with tagged polymer organic binder were analyzed using a Leica SP2 confocal laser scanning microscope (CSLM). The technique of labeling and CSLM analysis can be found elsewhere [7]. In this case the suspensions of Bentonite were done in a 10% w/w solution of NaCl for the three conditions studied.

3 RESULTS AND DISCUSSION

Pelletization

The pelletization results comparing the three conditions bentonite without organic binder and the bentonite versus bentonite and the two different organic binders can be found in Table 1 and Figure 1. The utilization of Alcotac™ CS increases the mechanical strength of the pellets in a ratio between 2,6 and 4,2 times higher than the strength obtained with Standard HPAM binder.

Table 1. Iron ore pelletization results.

	Dry Strenght (N)			Increase in strength due to organic binder addition (N)		Ratio of strength Increase
Bentonite Addition (%)	Only Bentonite	Std. HPAM (220g/t)	Alcotac™ CS (220g/t)	Std. HPAM	Alcotac™ CS	Alcotac™ CS / HPAM
0,22%	8,0	10,7	19,1	2,7	11,1	4,2
0,34%	11,1	16,9	26,2	5,8	15,1	2,6
0,49%	11,1	16,9	27,6	5,8	16,5	2,8
0,56%	19,1	24,9	34,2	5,8	15,1	2,6
0,67%	30,7	30,7	37,8	0,1	7,1	very high

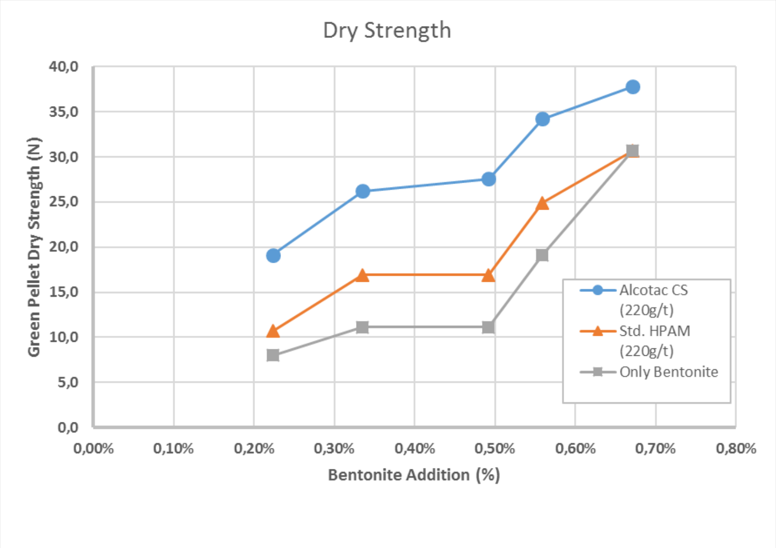

Figure 1. Dry strength of pellets obtained from agglomeration experiments.

Microscopy Analysis

Figure 2 shows a comparison between the microstructures produced after drying the bentonite suspensions. Note the scaffold-type bentonite structure obtained with Alcotac™ CS compared to the smooth surface of the dried bentonite without organic binder addition.

The focused ion beam cut (FIB, Figure 3) shows the difference in porosity inside the particles of dried bentonite. The bentonite without polymer organic binder exhibits a dense packing of the bentonite (Figure 3B and 3C) compared to the highly porous structure obtained in the case of bentonite with addition of Alcotac™ CS (Figures 3E and 3F).

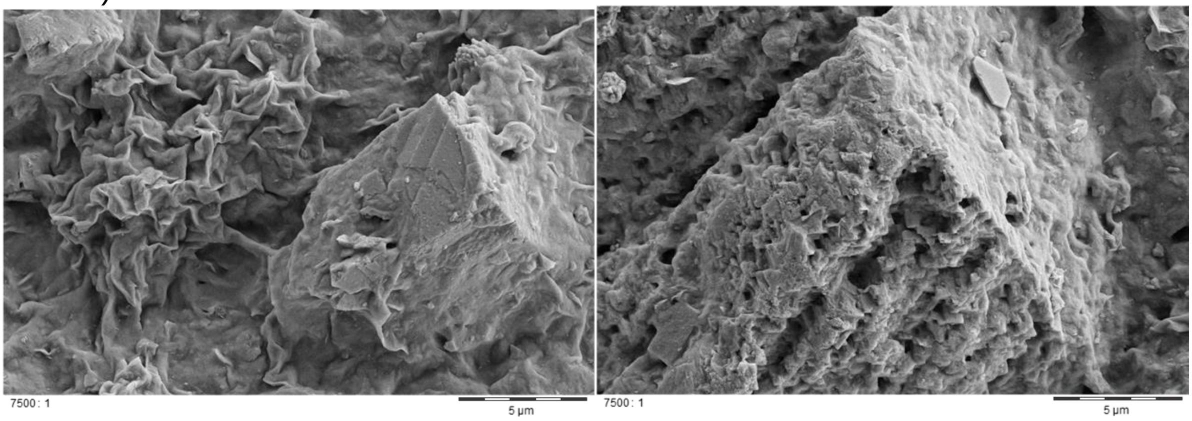

Figure 2. SEM photomicrographs of dried bentonite (left) and bentonite plus Alcotac™ CS (right). The dimensions taken from the pictures according to the scale bar in vertical direction are to multiply by a factor of 1.27 (tipping angle compensation).

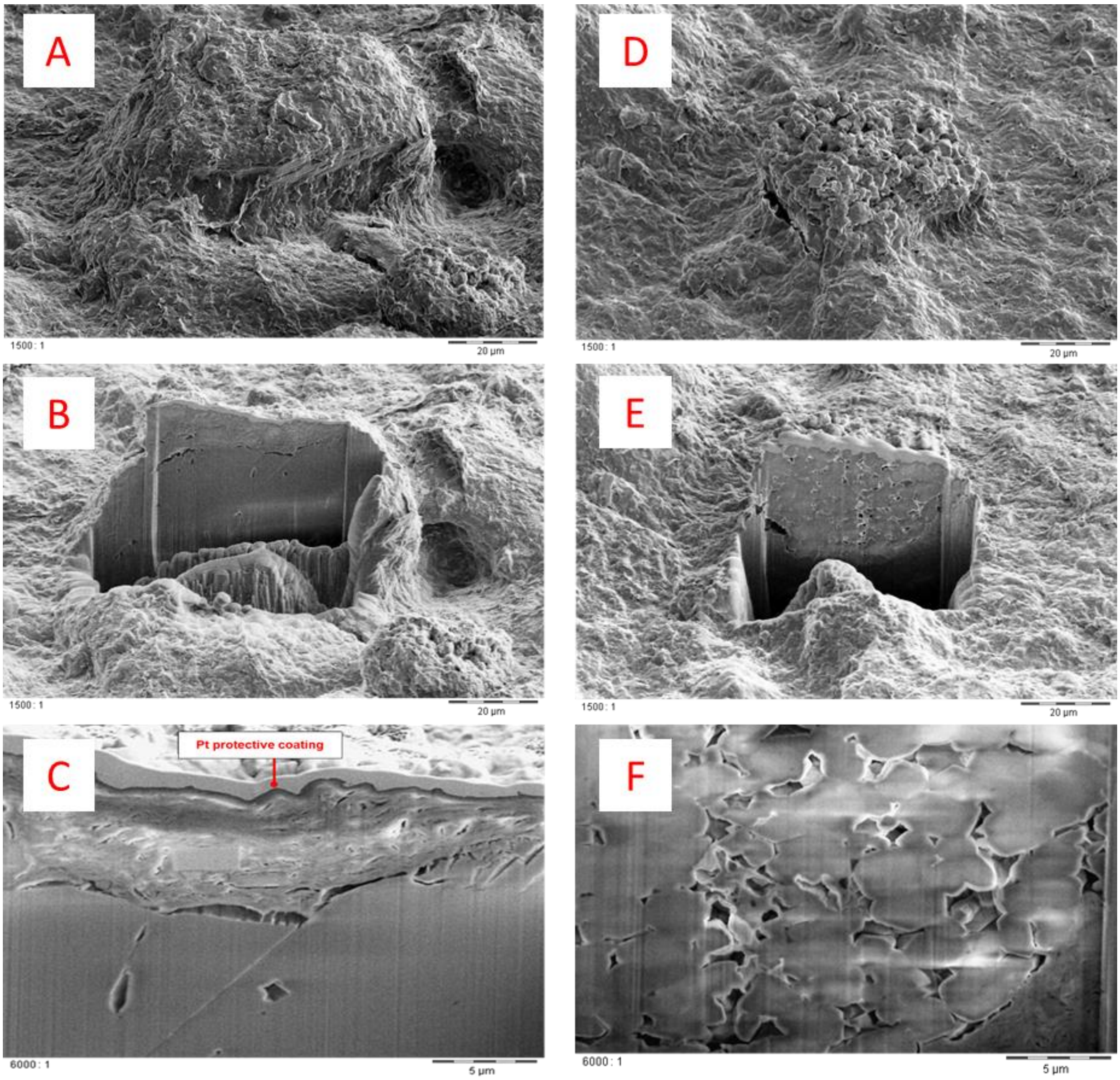

Figure 3. SEM+FIB photomicrographs of dried bentonite without organic binder (A, B and C) and bentonite plus Alcotac™ CS. Images A and D were taken before cutting with the focused ion beam and can be compared with B and E after the cut. The detail about the Pt protective coating is depicted in image C.

During the laser-confocal microscopy imaging, the particle of bentonite in liquid suspension can be analyzed to detect the presence and localization of a very small amount of molecules tagged with a fluorescent dye, with an extremely high resolution. In the images presented here, each image is shown in two parts: an image obtained with reflected illumination light and a second made with the fluorescent light emitted from the dye-tagged molecules.

The image of bentonite suspension without organic polymer binder is shown in Figure 4. This condition is the reference and the bentonite platelets are clearly dispersed in the suspension. The fluorescent image (right) shows the bentonite sample used does not exhibit self-fluorescent properties.

With the addition of Standard HPAM binder (Figure 5, left image), the bentonite particles seem to agglomerate forming a floc-type structure. The fluorescent image on Figure 5-right, shows the presence of dye-tagged molecules, but these seem to be concentrated in specific areas on the periphery of the floc structure formed. This is an indication of a low degree of interaction between the bentonite and the Standard HPAM polymer rather than flocculation of the particles.

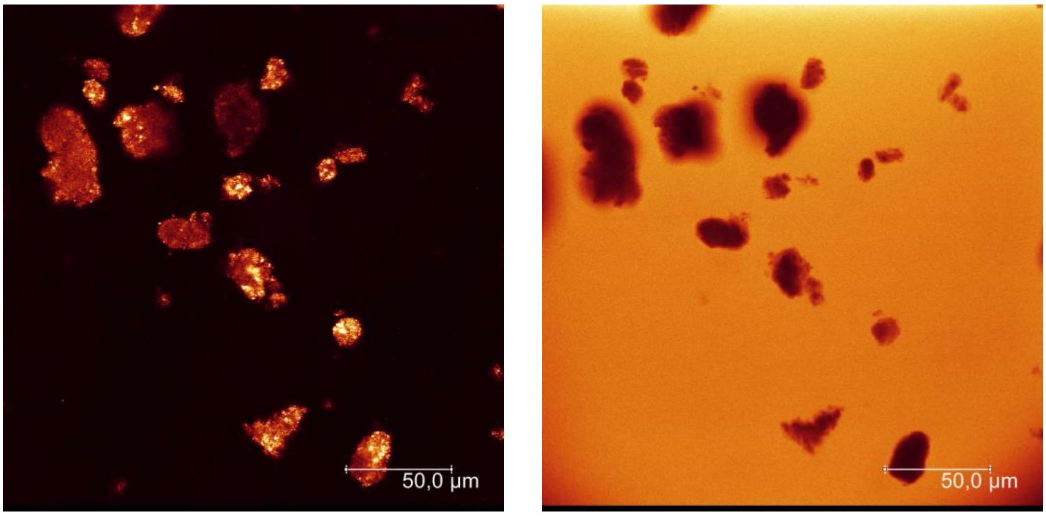

Figure 4. CLSM images of bentonite suspension without organic binder addition. Left: reflected light. Right: emitted fluorescence.

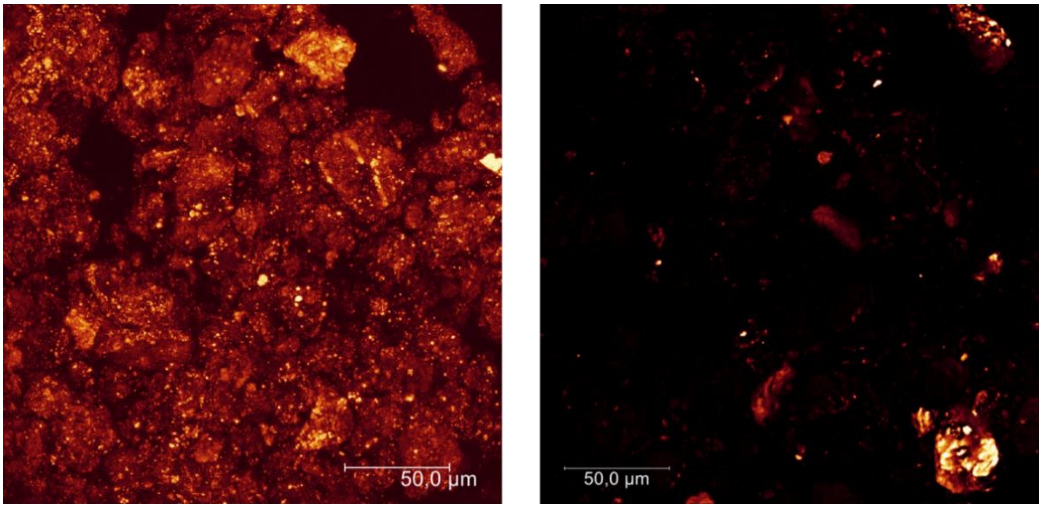

Figure 5. CLSM images of bentonite suspension with Standard HPAM polymer binder added. Left: reflected light. Right: emitted fluorescence.

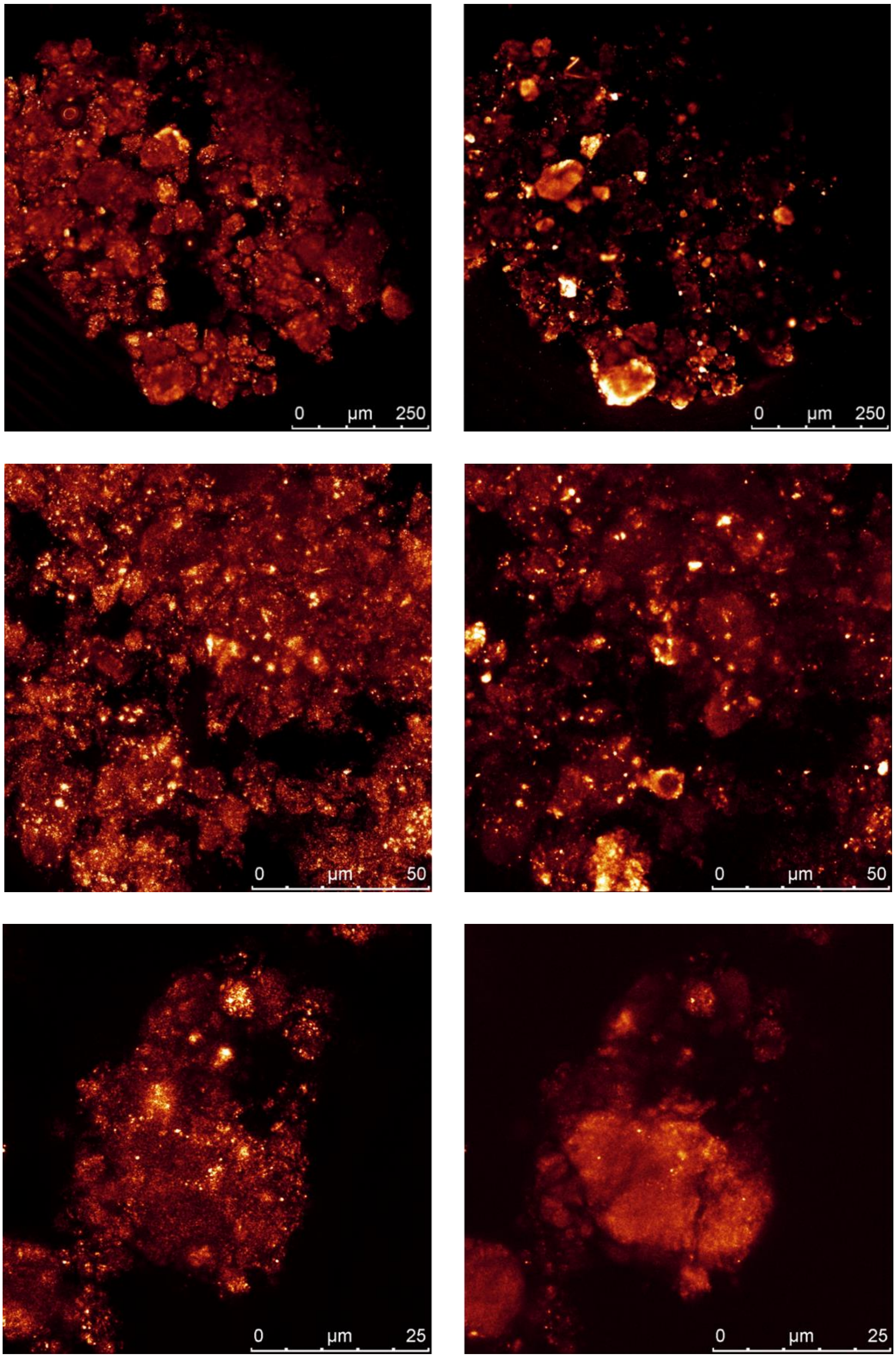

Figure 6. CLSM images of bentonite suspension with Alcotac™ CS polymer binder added. Left: reflected light. Right: emitted fluorescence.

Figure 6 shows CLSM images at different magnifications of bentonite used in combination with Alcotac™ CS (left side images). The floc-type structure is also obtained like in the case of Standard HPAM. However, from the fluorescence images (right side), the degree of adsorption of the Alcotac™ CS molecules are much higher than Standard HPAM and it is not only limited to the outer areas of the floc but it is found in the entire the surface of the bentonite. This unique high level of adsorption is congruent with the SEM structures and serve as a hypothesis to explain the superior mechanical properties of the pellets produced with Alcotac™ CS and bentonite.

4 CONCLUSION

The polymers analyzed show an increase in the mechanical strength of green pellets when added to bentonite as a binder system. In particular, the novel binder from BASF Alcotac™ CS exhibits a significantly higher degree of interaction with bentonite, when compared to a Standard HPAM. The interpretation of the SEM-FIB and CLSM images prove to be congruent with the superior mechanical properties of the pellets made with the novel binder Alcotac™ CS.

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