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Investigation of Used Motor Oil Regeneration Efficiency with Acid, Alkali and Combined Activation of Goshica's (Kosovo) Bentonite

Arjan Korpa*[1], Sara Dervishi[1], Diana Gecaj[1], Kristi Shahu[1], Spiro Drushku[2]
[1]University of Tirana, Faculty of Natural Sciences, Department of Chemistry, Tirana, Albania
[2]University of Tirana, Faculty of Natural Sciences, Department of Industrial Chemistry, Tirana, Albania

Abstract. Goshica's (Kosovo) bentonite was activated with three activation methods, namely, acid, alkaline and combined acid-alkaline activation, and their regeneration efficiency of used motor oil (UMO) having run about 15,000-20,000 km was evaluated. Optimal activation conditions of Goshica's bentonite with the employed oil and each of the three activation methods were found out. Bentonite samples were characterized using X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), X-ray fluorescence (XRF), as well as cation exchange capacity (CEC), surface and porosity properties before and after treatment with all three methods. Activation of bentonite brings about significant structural changes (specific surface area, pore size and volume) that depend on activation conditions and parameters, which can be predictive of the bentonite's oil regeneration efficiency. Goshica's bentonite activated by the combined method in the totality of the performance shows the best efficiency for the UMO regeneration.

Keywords: Goshica's (Kosovo) bentonite; acid, alkaline and combined activation; UMO regeneration efficiency

Introduction

With time and because of usage, the engine lubricating oil deteriorates and gets contaminated by contaminants and impurities resulting from undesirable oxidation and other processes, hence it will lose efficiency. At some point, the used lubricating oil needs to be changed and the replaced oil might end up as waste. The European directives urge for better management of resources and search for means to recover waste, i.e., the used motor oils (UMO). The Directives 75/439/EEC and 87/101/CE give priority to the recovery method, whereas incineration is accepted as a last alternative in case none of the others can be applied. Oil recovery via regeneration mostly employs clay minerals, because of their efficiency, attractive cost, ease of operation and availability (Amer, Khalili, & Awwad, 2010; Murray, 1991). Bentonites are the mostly used type of clays (montmorillonite ones) for UMO regeneration because of their suitable physico-chemical properties. The largest bentonite deposits in South East Europe are located in Kosovo, near the region of Vitia and Kamenica, including various areas such as Goshica, Sadovina and Jerlive, Karaqeva, etc. Based on the exploration activities carried out during 1970, the site near Vitia is estimated to hold over 100 million tonnes of bentonite reserves. In general, the natural clays have poorer regenerating activity (Richardson, 1978), therefore, acid activated and, in few cases, alkaline activated clays are employed for oil regeneration (Aguilar et al., 2020; Rosa et al., 2020; Salawudeen et al., 2014; Aishat et al., 2015). The activation process of bentonite causes beneficial changes in the chemical and mineralogical structure; hence they have better regenerating efficiency compared to natural active bentonites (Jovanović & Janaćković, 1991; Ravichandran & Sivasankar, 1997). Clay activation is applied to increase its adsorption properties depending on the activation conditions (Kuenzel et al., 2012). The activation process of bentonites increases their interlayer space (Komadel et al., 1997; Amari et al., 2010). There are two types of bentonites in nature: sodium or Wyoming bentonites that contain more sodium than

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*Corresponding Author

calcium and high calcium bentonites with calcium located in the structure of the layer as an exchangeable cation (Grim, 1978). The treatment of sodium bentonites with inorganic acids replaces calcium ions with monovalent hydrogen ions (Jozefaciuk & Bowanko, 2002; Dananaj, Frankovská, & Janotka, 2005), whereas calcium bentonites can be converted to sodium bentonites through alkali treatment (Alther, 1986; Rifai, Shaban, & Holail, 2001). In all cases a modification of the surface properties, porosity, type and concentration of exchangeable ions is noticed after the clay activation (Cui, 2017). Bentonite activation with inorganic acids changes their surface properties and smectite structure, and forms poorly crystalline gel type products (Guo et al., 2016; Liu et al., 2012; Wang et al., 2017), which on the other hand affect their adsorption and catalytic properties (Tha-In, Dau, & Dumri, 2013; Komadel et al., 1997; Tyagi, Chudasama, & Jasra, 2006; Aguilar et al., 2020; Rosa et al., 2020). Aguilar et al. treated Ecuadorian bentonite with sulfuric and acetic acid at respectively 10, 40 and 60% (weight ratios) (Aguilar et al., 2020). Both acids showed a similar bentonite structure transformation, causing cations leaching of the intermediate layer. The bentonite activated with sulfuric acid 40 v/w% and sulfuric/acetic acid (1:1 ratio) enabled the highest regeneration of the UMO, by reducing its viscosity, acidity and alkalinity respectively 23%, 80% and 29%. Furthermore, Afolabi et al. (2016) reported that clays activated with sulfuric acid increase their specific surface area 22 times and their adsorption capacity 6 times. Acid percentage of 20% and adsorbent percentage of 15% are optimum bentonite activation conditions (Kulkarni, 2017) for highest regeneration efficiency. According to Yildiz and Çalimli (2002), the structure changes depend on the exchangeable cations, the type of clay and the ratio of the additive; bentonite properties could be tailored through treatment with inorganic acids (Yildiz & Çalimli, 2002). Alkali activation of bentonite is generally carried out with sodium carbonate and sodium or potassium hydroxide (Provis & Van Deventer, 2009; Salawudeen et al., 2014; Rosário et al., 2010; Belver, Bañares Muñoz, & Vicente, 2002). All activation conditions i.e., alkali concentration and type, temperature, contact time, alkali/clay ratio, pH, particle size, etc. affect the adsorption capacity of bentonite, and the reaction products formed are either crystalline zeolite (Cundy & Cox, 2005) or an alkali aluminosilicate hydrate gel framework (Duxson et al., 2007). Finally, the increase in oil regenerating capacity of bentonites depends on the activation conditions and parameters (acid or alkali concentration, alkali or acid/clay ratio, temperature, contact time, particle size, bentonite composition and other factors. After regeneration the oil can be turned into a product to be reused as a base oil or as a fuel in the engines of transport vehicles or industrial machinery. The present paper aims to investigate the effectiveness of acid, alkaline and combined acid - alkaline activation of representative bentonite samples obtained from the Goshica's deposits in properties regeneration of a UMO. To our knowledge, the combined acid - alkaline activation of bentonite for the purpose of used oil regeneration has not been investigated so far. Its effectiveness will be compared with that of acid and alkaline activation. Optimal activation conditions of Goshica's bentonite with the employed oils and each of the three activation methods should be found out.

Materials and Methods

Materials

The bentonite of Kosovo (Goshica region) is employed as raw material. All chemicals used were from Merck manufacturing company; H_2SO_4 (98%) with density d = 1.835 g/cm^3, CH_3COOH (95%) with density 1.05 g/cm^3, and distilled water was used. For activation of the bentonite in laboratory conditions, a 3-nozzle balloon with a round bottom and volume of 2 liters was used. The balloon is equipped with a thermometer, stirrer and a reflux condenser (for condensing the vapors and returning them to the balloon). The balloon is placed on a heating magnetic mixer with 150 rpm. Sufficient amounts of a used motor oil (UMO) sample were employed; this sample is made of mixed (mineral and synthetic) oil that had been running for approximately 15000 – 20000 km. The UMO employed in these experiments has been collected from a local service station barrel where the oil change takes place. Their properties before and after treatment with the activated bentonite have been compared with these of two reference oils; a new oil of type SAE 5W-30 with additives and a basic oil of type SN 90 without additives.

Methods

The bentonite was initially washed to remove unnecessary components contained in it, such as sand, etc. by successive decantation. After decantation, the sludge was filtered with a sparse filter into the Büchner funnel with water pump. The obtained paste was placed in an open container and dried at room temperature. The resulting mass was ground into powder in a porcelain mortar, then crushed and passed through a sieve with a mesh size of 20 mesh (841 microns). After adding the amount of bentonite and sulfuric acid solution, the balloon is closed and the magnetic mixer is activated. After the onset of boiling the acid activation lasted 2 hours. At the end of activation, the suspension is filtered in the Büchner funnel under vacuum. The bentonite is purified from acid by rinsing it with distilled water preheated to 70°C. Complete washing of the clay is checked with a $BaCl_2$ indicator until sulfate ions cannot be detected. It is then dried at 110°C and reground. Activation of bentonite was carried with sulfuric acid (98%), at 10%, 30% and 50% (25%:25% for the mixture of sulfuric acid (98%) with acetic acid (95%)) referring to the bentonite dry mass (dried for 24 hours at 110°C). Table 1 shows all suspensions used for acid activation.

Table 1. Suspensions used for acid activation

Acid/bentonite % (dry mass)	**10%**	**30%**	**50%**	**25%+25%**
Bentonite (g)	240	240	240	240
H_2SO_4 (ml)	14.6	56.1	130.8	65.4
CH_3COOH (ml)	0	0	0	114.3
H_2O (ml)	1893	1817	1700	1680

Alkali activation of bentonite was carried with sodium carbonate at concentrations of 10%, 30% and 50% (25%: 25% for the mixture of sodium carbonate with sodium hydroxide) referring to the bentonite dry mass (dried for 24 hours at 110°C). In this process the activation time was 3 hours and the activation temperature 200°C. At the end of activation, the suspension is filtered in the Büchner funnel under vacuum. The bentonite is purified from alkalies by rinsing it with distilled water preheated to 70°C. Complete washing of the bentonite is checked with a $AgNO_3$ indicator until chlorur ions cannot be detected. It is then dried at 110°C and reground. Table 2 shows all suspensions used for the alkaline activation.

Table 2. Suspensions used for alkaline activation

Alkali/bentonite % (dry mass)	**10%**	**30%**	**50%**	**25% + 25%**
Bentonite (g)	240	240	240	240
Na_2CO_3 (g)	26.8	102.9	240	120
NaOH (g)	0	0	0	120
H_2O (ml)	1893	1817	1700	1700

The combined activation consisted in firstly treating the bentonite with acid and following all steps and treatments as for the acid activation above. After drying and regrinding, the bentonite was treated with alkalis and the same procedure and steps as for the alkaline activation described above, was followed. All suspension used for the combined activation are shown in Table 3.

Table 3. Suspensions used for combined activation (acid and alkaline)

Bentonite (g)	**240**	**240**	**240**	**240**
H_2SO_4/bentonite (dry mass) (%)	50	50	50	50
Na_2CO_3/bentonite (dry mass) (%)	10	30	50	0
$CaCl_2$/bentonite (dry mass) (%)	0	0	0	50
H_2O (ml)	1893	1817	1700	1680

The cation exchange capacity (CEC) was determined following the ammonium acetate method of Schollenberger and Dreibelbis (1930) at pH 7 (Ross & Ketterings, 2011); the concentration of NH_4-N in KCl solution was determined by distillation.

$$\text{CEC (cmolc / kg)} = ((NH_4\text{-}N_{\text{in extract}} - NH_4\text{-}N_{\text{in blank}}) / 18$$

Calculations:

$\text{CEC \% } NH_4^+ = [(a-b) \times N \times f \times 1.4007] \times 100/m$

a – blank sample 25 ml

b – titred amount NaOH in ml

N - normality 0.1

f – correction factor

m – bentonite amount in g

$\% NH_4^+ \times 1000 = \text{CEC mg } NH_4^+$

$\text{CEC (meq/100g)} = m \times \text{valence}/M$

m – amount of NH_4^+ in mg

M – molar mass of $NH_4^+ = 18$

An IRAFINITY Shimatzu, Fourier Transform infrared spectrophotometer was used to determine the chemical composition of the bentonite.

An Instruments Quantachrome NOVA 1200e (USA) was used to determine the surface and volume properties based on nitrogen uptake at 77.4 K. Prior to measurements, samples were passed at 150°C for 16 hours. The adsorption-desorption isotherms were analyzed: Vt and Dav were evaluated according to the Gurvich method at relative pressures close to 0.99, Vmi, Smi and Sext were evaluated according to the V - t method (Boer, 1965). The Barett-Joyner-Halenda method was used to calculate the pore size distribution (PSD) (Barrett, Joyner, & Halenda, 1951).

A Bruker D8 Advance diffractometer with Cu Kα radiation and the LynxEye detector was employed for the X-ray measurements. The X-ray diffraction patterns of the sample dust were collected within the range of 5.3 to 80° 2θ with a constant step of 0.02° 2θ and the counting time 52.5 sec / open. Phase identification was performed with Diffracplus EVA using the ICDD-PDF2 database (2014).

Oil Regeneration Experiments

The bentonite-used oil mixture was added to the round bottom balloon equipped with a magnetic mixer and heated at two temperatures; 90°C for 60 min and 120°C for 90 min by constantly stirring. After the specified treatment time, the treated bentonite was filtered on medium pore filter paper. This process produced yellow oil and an amount of sludge not very different from the initial weight of bentonite used. This treated and filtered oil was determined its density at 15°C according to (EN ISO 3675), kinematic viscosity at 100°C according to (EN ISO 3104), kinematic viscosity at 40°C according to (EN ISO3104), viscosity index (ISO 2909), sulfur content in % (m/m), pour point according to (ISO 3016), and color (EN ISO 2049).

The pour point was analyzed by the pour point apparatus (ASTM D97) in which 20 ml of the oil samples were introduced into a test tube, and then the samples were cooled very rapidly at a specific rate. The temperature at which certain hydrocarbons (paraffin) began to turn into crystalline form is called mist or cloud spots. Upon further cooling, the oil samples stopped flowing and this temperature is called the pouring point of this oil.

Results and Discussion

The XRF results (not shown here for manuscript length concerns) show that all percentages of metal oxides decrease with increasing acid concentration. Reduction of MgO and Al_2O_3 values indicate that the Mg^{2+} and Al^{3+} cations of the octahedral layer are exposed to acid and begin to digest (Mejia, 2013). There is also a decrease of the percentage of Na_2O and K_2O oxides; these ions are found in the space between the layers of clay. In Tables 4-6 are shown the cation exchange capacity (CEC), specific surface area (Ssp), total pore volume (Vt), average diameter (Dav), micropore volume (Vmi), micropore surface area (Smi), and external surface area (Sext) of the bentonite before and after treatment with all three methods. It is noted that with all three activation methods, in general all CEC, Ssp, Vt, Smi and Sext increase with increasing acid(s) and alkali(s) concentration. In line with the above, a decrease of the average pore diameter (Dav) is noted. The highest values of CEC, Ssp, Vt, Smi and Sext are reached for combined activation, especially the combined bentonite treatment, initially with 50% H_2SO_4 followed by 50% $CaCl_2$. All CEC, Ssp, Vt, Smi and Sext are important parameters that predict the oil regenerating capacity of the bentonite (Komadel & Madejová, 2006; Huang, Sato, & Aida, 2017). In line with the above, it is expected that the bentonite samples with the highest CEC, Ssp, Vt, Smi and Sext values will represent better regenerating oil efficiency.

Table 4. Cation exchange capacity (CEC), surface and volume properties of untreated bentonite and after treatment with acid activation

Activator/bentonite % (dry mass)	Cationic exchange capacity (CEC)	Specific surface area (Ssp)	Total pore volume (Vt)	Average diameter (Dav)	Micropore volume (Vmi)	Micropore surface area (Smi)	External surface area (Sext)
	meq/100g	**m2/g**	**cm3/g**	**nm**	**cm3/g**	**m2/g**	**m2/g**
0%	30.25	81	0.12	6	0.003	8	73
H_2SO_4 10%	42.36	85	0.13	6	0.003	7	78
H_2SO_4 30%	47.81	69	0.13	7.6	0.002	5	64
H_2SO_4 50%	53.79	162	0.2	4.8	0.010	25	137
H_2SO_4 25% + CH_3COOH 25%	50.79	97	0.14	5.4	0.005	12	85

Table 5. Cation exchange capacity (CEC), surface and volume properties of untreated bentonite and after treatment with alkaline activation

Activator/bentonite % (dry mass)	Cationic exchange capacity (CEC)	Specific surface area (Ssp)	Total pore volume (Vt)	Average diameter (Dav)	Micropore volume (Vmi)	Micropore surface area (Smi)	External surface area (Sext)
	meq/100g	**m2/g**	**cm3/g**	**nm**	**cm3/g**	**m2/g**	**m2/g**
0%	30.25	81	0.12	6	0.003	8	73
Na_2CO_3 10%	63.53	83	0.11	5.4	0.004	9	74
Na_2CO_3 30%	78.66	71	0.11	6.3	0.004	9	62
Na2CO3 50%	104.59	73	0.11	6.1	0.004	10	62
NaOH 25% + Na_2CO_3 25%	78.66	59	0.12	8	0.001	2	57

Table 6. Cation exchange capacity (CEC), surface and volume properties of untreated bentonite and after treatment with combined activation (acid and alkaline)

Activator/bentonite % (dry mass)	Cationic exchange capacity (CEC)	Specific surface area (Ssp)	Total pore volume (Vt)	Average diameter (Dav)	Micropore volume (Vmi)	Micropore surface area (Smi)	External surface area (Sext)
	meq/100g	**m2/g**	**cm3/g**	**nm**	**cm3/g**	**m2/g**	**m2/g**
H_2SO_4 50% + Na_2CO_3 10%	114.97	111	0.16	5.8	0	0	111
H_2SO_4 50% + Na_2CO_3 30%	96.81	97	0.16	6.5	0.007	17	80
H_2SO_4 50% + Na_2CO_3 50%	121.02	122	0.19	6.2	0.009	21	101
H_2SO_4 50% + $CaCl_2$ 50%	135.08	150	0.21	5.6	0.004	11	139

Figures 1-3 show the X-ray diffraction (XRD) patterns of bentonite before and after treatment with all three activation methods. A significant difference between all patterns is the amount of carbonate minerals (calcite) that continuously decreases while that of sulfate minerals (gypsum and anhydrite) increases with the increase of the acid amount used for activation.

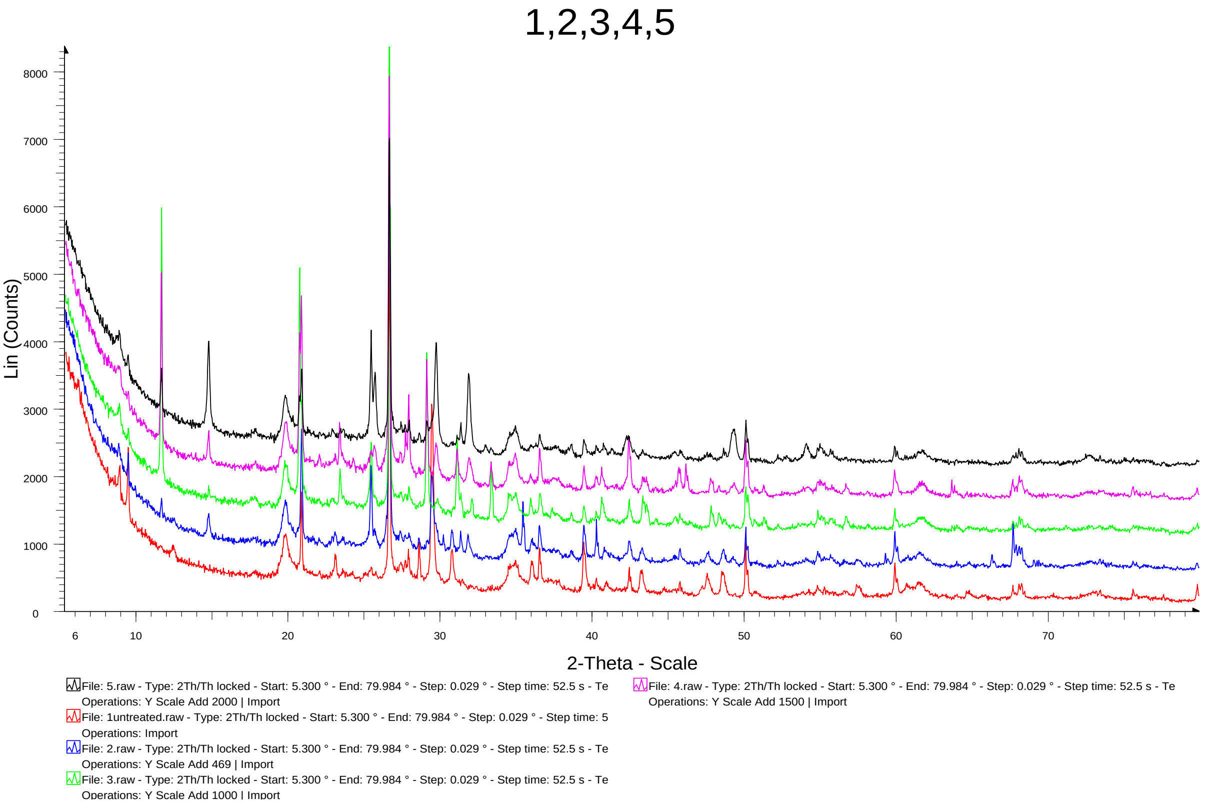

Figure 1. XRD patterns of bentonite before treatment (red color) and after treatment with respectively 10% (blue color), 30%, 50% H_2SO_4 and 25% H_2SO_4 + 25% CH_3COOH (black color)

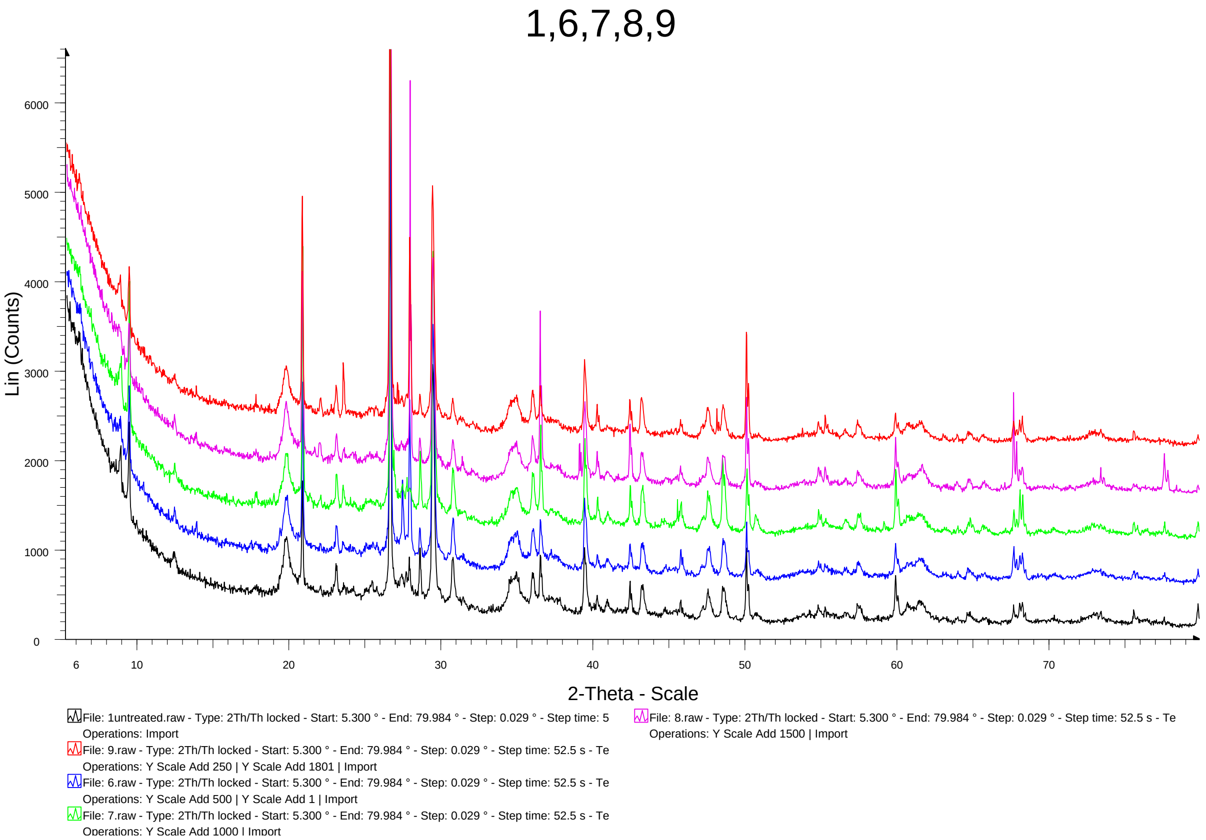

Figure 2. XRD patterns of bentonite before treatment (black color) and after treatment with respectively 10% (blue color), 30%, 50% Na_2CO_3 and 25% H_2SO_4 + 25% NaOH (red color)

Bentonite samples treated with different amounts of Na_2CO_3 and NaOH did not show any significant change in composition compared to the untreated sample.

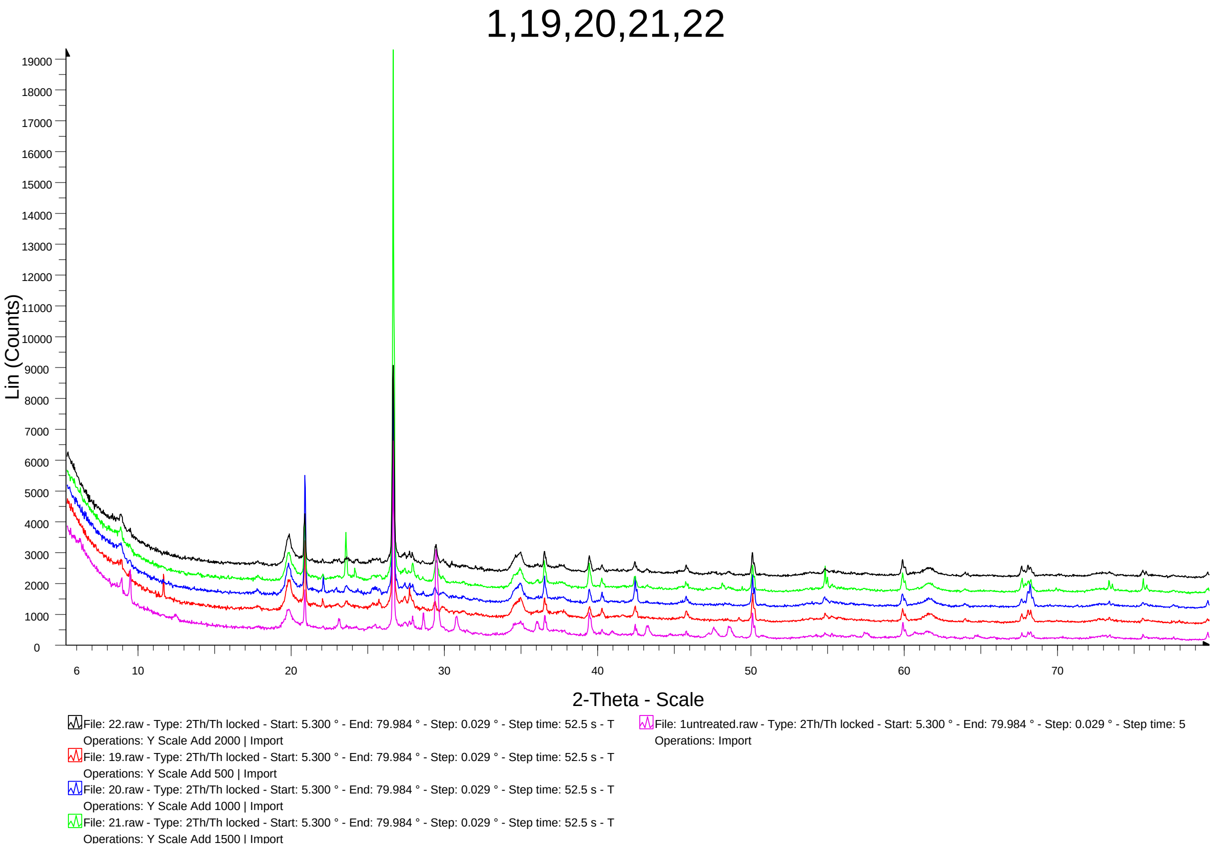

Figure 3. XRD patterns of bentonite before treatment (pink color) and after treatment with respectively H_2SO_4 50% + Na_2CO_3 10% (red color), H_2SO_4 50% + Na_2CO_3 30%, H_2SO_4 50% + Na_2CO_3 50% and H_2SO_4 50% + $CaCl_2$ 50% (black color)

Bentonite samples treated with different amounts of H_2SO_4 and $CaCl_2$ or Na_2CO_3 show a decrease in the percentage of carbonate compounds but without the formation of new phases. Figure 4 shows the Fourier Transform Infrared Spectroscopy (FT-IR) spectra for the bentonite before and after activation with all three methods. The FT-IR spectrum of untreated bentonite shows a band at 3600 cm^{-1} in the OH extension region, which is dedicated to the hydroxyl groups coordinated in the octahedral cations (Madejová, Komadel, & Čičel, 1994). The band 3620 cm^{-1} is due to the hydroxyl group attached to the Al^{3+} cations (Vicente-Rodríguez et al., 1996). The bands of region 670 - 780 cm^{-1} indicate the presence of quartz mixtures present in the sample (Tyagi, Chudasama, & Jasra, 2006). The region between 870 - 980 cm^{-1} is dominated respectively by the Si-O-T bands (T = tetrahedral Si or Al) of the mineral phases of clay and aluminosilicate. The low-intensity band in 1635 cm^{-1} can be assigned to OH deformation due to the presence of interstitial water (Tyagi, Chudasama, & Jasra, 2006; Sidhoum et al., 2013). The band at 1481cm^{-1} is present due to calcite impurity (Temuujin et al., 2004). The absorption of about 2150 cm^{-1} is due to the vibrating of Al – OH group. Its location depends on the content of montmorillonite, illite and kaolinite phases in clay (Ducasse et al., 2020). The FT-IR spectrum of bentonite treated with sulfuric acid shows that the vibration intensity of the hydroxyl curvature of about 870 cm^{-1} decreases with increasing acid concentration, indicating the leaching of cations of Ca, Mg and Fe with increasing acid concentration (Tyagi, Chudasama, & Jasra, 2006). After treatment with acid, it is expected that Ca^{2+} and Mg^{2+} ions are more prone to acid attack. Moreover, the shape of the Si-O alignment band at 1001 cm^{-1} shows Si changes after acid treatment with increasing concentrations. Quartz band at 671 cm^{-1} shows an increase in intensity after treatment that correlates with increased acid concentration. At lower sulfuric acid concentrations, the dissolution of tetrahedral silica from the clay structure does not occur. Fernández-Jiménez and Palomo (2005) reported that in most cases, clay-based activation results in a decrease in the dominant bandwidth position as a result of more Si-O-Al bonds compared to the number of Si-O-Si bonds in the aluminosilicate framework (Fernández-Jiménez & Palomo, 2005). According to Shaqour, Ismeik, and Esaifan (2017), the spectra of base-activated materials show an extraordinary decrease in the intensity of the Al-O bending modes and the O-H region stretching modes, with increasing Na_2CO_3 (Shaqour, Ismeik, & Esaifan, 2017). In full accordance with Shaqour Ismeik, and Esaifan (2017), it was found that increasing the Na_2CO_3 concentration leads to a continuous decrease in the band intensity of 2360 cm^{-1}.

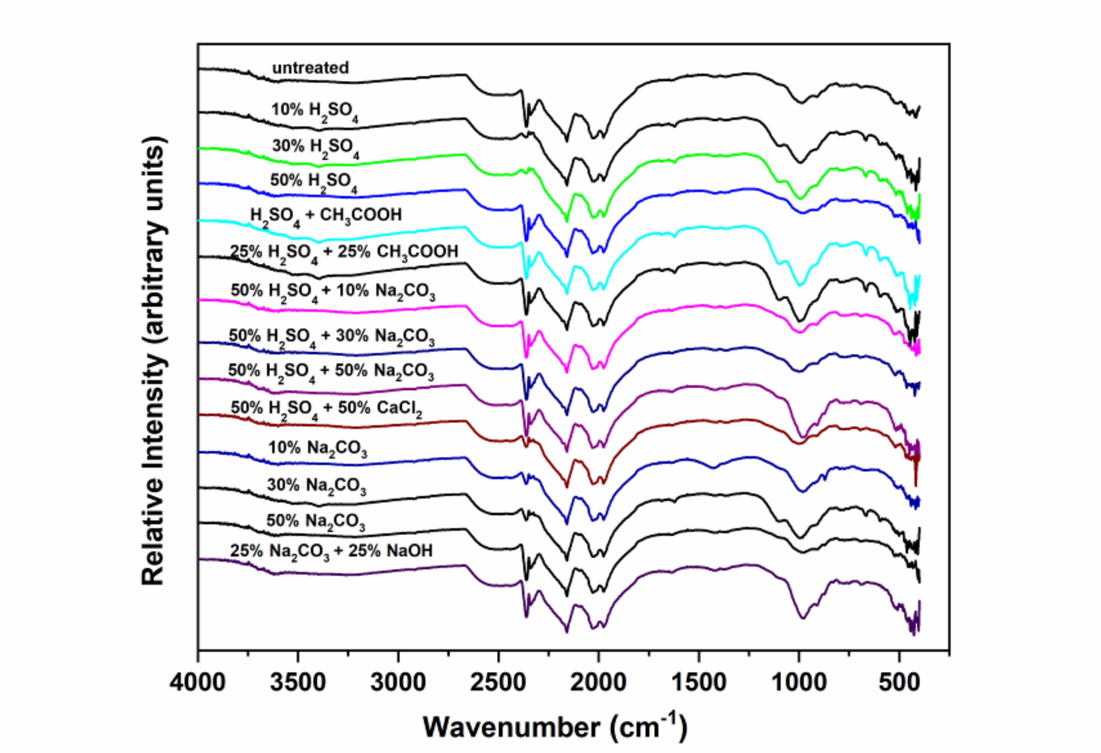

Figure 4. FTIR spectra of untreated and treated bentonite treated with acid(s), alkali(s) and the combined method (acid(s) and alkali(s))

The UMO that was treated with activated bentonites, was further filtered and its density at 15°C based on EN ISO 3675, kinematic viscosity at 100°C based on EN ISO3104, kinematic viscosity at 40°C based on EN ISO3104, viscosity index based on ISO 2909, sulfur content in % (m/m) and pour point based on ISO 3016 were determined. These data together with the “standard” values of the new reference oils are presented in Tables 7 and 9. Based on the results of Tables 7-10, it can be generally concluded that the parameters of the UMO have been improved and the best values were obtained with the bentonite samples that were activated with 50% H_2SO_4, 50% H_2SO_4 + 50% $CaCl_2$ and 50% H_2SO_4 + 50% Na_2CO_3.

Table 7. Comparison of the tested parameters of new motor oil with additives, new motor oil without additives, UMO (15000 - 20000 km) before and after treatment with activation method at 90°C for 60 minutes

Sample name	Density at 15 °C (EN ISO 3675)	Kinematic viscosity at 100 °C (EN ISO3104)	Kinematic viscosity at 40 °C (EN ISO 3104)	Viscosity index (EN ISO 2909)	Sulphur % (EN ISO 8754)	Pour point (EN ISO 3016)
New oil with additives (SAE 5W-30) (reference) reported by producer	0.840-0.860	11.3-12.3	7.9-9.5	>165	<0.5	<-33
New oil with additives (SAE 5W-30) (reference) measured values	0.834	12.1	72.5	>165	0.12	-30
New oil without additives (SN90) (reference) reported by producer	any	>5.80	>31.5	>120	<0.03	<-26
New oil without additives (SN90) (reference) measured values	0.843	6.2	35	126	0.20	-18
UMO untreated and unfiltered	0.8673	9.17	50.23	167	0.186	-40
UMO treated with unactivated bentonite	0.8494	6.7	29.8	199	0.126	-35

Table 8. Comparison of the tested parameters of UMO (15000 – 20000 km) that has been treated at 90°C for 60 minutes with bentonite previously activated with all three methods (acid(s), alkali(s) and combined acid(s) + alkali(s)

Sample name	Density at 15 °C (EN ISO 3675)	Kinematic viscosity at 100 °C (EN ISO3104)	Kinematic viscosity at 40 °C (EN ISO 3104)	Viscosity index (EN ISO 2909)	Sulphur % (EN ISO 8754)	Pour point (EN ISO 3016)
UMO treated with activated bentonite (10% H_2SO_4/bentonite)	0.8424	10.3	58.8	165	0.166	-39
UMO treated with activated bentonite (30% H_2SO_4/bentonite)	0.8496	10.87	61.67	169	0.159	-38
UMO treated with activated bentonite (50% H_2SO_4/bentonite)	0.8473	10.48	59.38	168	0.163	-39
UMO treated with activated bentonite (25% H_2SO_4 + 25% CH_3COOH/bentonite)	0.8485	10.58	60.08	165	0.174	-38
UMO treated with activated bentonite (10% Na_2CO_3/bentonite)	0.8506	6.08	28.8	166	0.127	-39
UMO treated with activated bentonite (30% Na_2CO_3/bentonite)	0.8498	8.96	28.45	311	0.126	-35
UMO treated with activated bentonite (50% Na_2CO_3/bentonite)	0.8492	5.98	28.45	163	0.117	-33
UMO treated with activated bentonite (25% Na_2CO_3 + 25% NaOH/bentonite)	0.8500	10.6	60.14	168	0.147	-39
UMO treated with activated bentonite (50% H_2SO_4 + 50% $CaCl_2$/bentonite)	0.8483	12.58	59.72	216	0.161	-39
V F -50% H2SO4 + 10%Na2CO3 90 °C, 60 min	0.8474	11.08	58.76	185	0.155	-39
V F 50% H2SO4 +30% Na2CO3 90 °C, 60 min	0.849	11.15	63.57	170	0.160	-38
V F 50% H2SO4 + 50%Na2CO3 90 °C, 60 min	0.8495	10.63	59.74	170	0.156	-39

Table 9. Comparison of the tested parameters of new motor oil with additives, new motor oil without additives, UMO (15000 - 20000 km) before and after treatment with activation method at 120°C for 90 minutes

Sample name	Density at 15 °C (EN ISO 3675)	Kinematic viscosity at 100 °C (EN ISO3104)	Kinematic viscosity at 40 °C (EN ISO 3104)	Viscosity index (EN ISO 2909)	Sulphur % (EN ISO 8754)	Pour point (EN ISO 3016)
New oil with additives (SAE 5W-30) (reference) reported by producer	0.840-0.860	11.3-12.3	7.9-9.5	>165	<0.5	<-33
New oil with additives (SAE 5W-30) (reference) measured values	0.834	12.1	72.5	>165	0.12	-30
New oil without additives (SN90) (reference) reported by producer	any	>5.80	>31.5	>120	<0.03	<-26
New oil without additives (SN90) (reference) measured values	0.843	6.2	35	126	0.20	-18
UMO untreated and unfiltered	0.8673	9.17	50.23	167	0.186	-40
UMO treated with unactivated bentonite	0.8505	6.22	27.62	186	0.132	-34

Table 10. Comparison of the tested parameters of UMO (15000 – 20000 km) that has been treated at 120°C for 90 minutes with bentonite previously activated with all three methods (acid(s), alkali(s) and combined acid(s) + alkali(s)

Sample name	Density at 15 °C (EN ISO 3675)	Kinematic viscosity at 100 °C (EN ISO3104)	Kinematic viscosity at 40 °C (EN ISO 3104)	Viscosity index (EN ISO 2909)	Sulphur % (EN ISO 8754)	Pour point (EN ISO 3016)
UMO treated with activated bentonite (10% H_2SO_4/bentonite)	0.8495	6.33	29.33	176	0.130	-33
UMO treated with activated bentonite (30% H_2SO_4/bentonite)	0.8490	6.96	28.1	225	0.128	-34
UMO treated with activated bentonite (50% H_2SO_4/bentonite)	0.8497	6.35	28.75	182	0.128	-32
UMO treated with activated bentonite (25% H_2SO_4 + 25% CH_3COOH/bentonite)	0.8487	6.16	28.83	170	0.128	-35
UMO treated with activated bentonite (10% Na_2CO_3/bentonite)	0.8500	9.29	27.79	348	0.124	-31
UMO treated with activated bentonite (30% Na_2CO_3/bentonite)	0.8538	6.81	27.31	225	0.062	-33
UMO treated with activated bentonite (50% Na_2CO_3/bentonite)	0.8501	6.21	27.91	182	0.091	-32
UMO treated with activated bentonite (25% Na_2CO_3 + 25% NaOH/bentonite)	0.8503	6.18	28.14	178	0.126	-34
UMO treated with activated bentonite (50% H_2SO_4 + 50% $CaCl_2$/bentonite)	0.8497	6.05	28.13	170	0.125	-33
V F -50% H2SO4 + 10%Na2CO3 90 °C, 60 min	0.8505	6.56	28.12	200	0.124	-33
V F 50% H2SO4 +30% Na2CO3 90 °C, 60 min	0.8509	6.08	28.61	167	0.129	-34
V F 50% H2SO4 + 50%Na2CO3 90 °C, 60 min	0.8505	6.58	29.25	191	0.160	-34

Tables 7 and 8 show the parameters of new motor oil with additives, type SAE 5W-30, new motor oil without additives, type SN 90 and tested parameters of used motor oil (UMO) with 15000-20000 km, before and after treatment with acid(s), alkali(s) and combined activation method at a temperature of 90°C for 60 minutes. The comparison of parameters of UMO before and after treatment with bentonite activated with acid(s), alkali(s), and by the combined method, were made with the parameters of reference oil without additives of type SN 90 and reference oil with additives of type SAE 5W-30. The density of new motor oil with additives of type SAE 5W-30 at temperature 15°C is 0.834g/cm^3, while the density of new reference oil type SN 90, without additives at same temperature is 0.843 g/cm^3. The best density values at 15°C are shown by the bentonite treated oil activated with 10% H_2SO_4, with a value of 0.8424 g/cm^3. Also, the bentonite treated oil activated with 50% H_2SO_4 + 10% Na_2CO_3 with a density value of 0.8474 g/cm^3. The viscosity of new reference oil without additives of type SN 90 compared to the viscosity values of bentonite-treated oil with three activation methods, represents an improvement in viscosity values. The best values are for the bentonite-treated oil with acid activation and the combined method. The reference oil viscosity index of oil without additives, type SN90 is 126, while that of untreated UMO is 167. Good results are presented by the viscosity index of UMO treated with bentonite that has been activated with 30% Na_2CO_3 (311), as well as UMO treated with bentonite that has been activated with 50% H_2SO_4 and 50% $CaCl_2$ and also UMO treated with bentonite that has been activated with 50% H_2SO_4 + 10% Na_2CO_3 at temperature 90°C for 60 minutes. Regarding the pour point, the results in Table 7 show that the pour point of the new motor oil with additives (SAE 5W-30) is -33°C, the pour point of the reference oil without additives (SN90) is -26°C, while the pour point of UMO is -40°C. From the comparison of the pour point of oil treated with non activated bentonite (-35) with the pour point of oil treated with activated bentonite with 50% Na_2CO_3 at a temperature of 90°C and duration 60 minutes (-33), there is some improvement of the pour point value in UMO treated with 50% Na_2CO_3. It is thought that this value is as a result of the oxidation of sulfur and its compounds leading to reductions up to values compared to those of the reference oil in Table 8. The data presented in Tables 7 and 8 show that the amount of sulfur present in the new motor oil with additives (SAE 5W-30) is 0.12% and in the reference oil without additives (SN90) is 0.005% (50 ppm), while the amount of sulfur of UMO is 0.186%. The sulfur content of the oil treated with non activated bentonite (0.126%) is compared with the content the sulfur of the UMO treated with activated bentonite with the three methods, at the temperature of 90°C for 60 minutes. It results that the values of sulfur of UMO treated with bentonite that has been activated with alkali(s) (10%, 30%, 50% Na_2CO_3) respectively 0.127%, 0.126%, 0.117%, represent better values than the UMO treated with bentonite that has been activated with acid(s) and by the combined method. Tables 9 and 10 show the tested parameters of new reference motor oil with additives of type SAE 5W-30, new reference oil without additives of type SN 90 and tested parameters of UMO, before and after treatment with acid(s), alkali(s) and combined activation method at 120°C for 90 minutes. The density of the new reference oil without additives of type SN 90 at 15°C is 0.843 g/cm^3. The best density values at 15°C are oil treated with bentonite activated with 10% H_2SO_4 (0.8458 g/cm^3), as well as oil treated with bentonite activated with 50% H_2SO_4 + 50% $CaCl_2$ (0.8455 g/cm^3) and oil treated with activated bentonite with 25% H_2SO_4 + 25% CH_3COOH (0.8455 g/cm^3). There is an improvement of viscosity of the UMO treated with activated bentonite with three activation methods as compared to the viscosity of the new reference oil without additives (type SN 90). The best values are UMO treated with activated bentonite with 10%, 30% and 50% Na_2CO_3, (respectively 6.31, 6.05 and 6.0) for kinematic viscosity at 100°C and (26.45, 28.55, 27.28) for kinematic viscosity at 40C. The viscosity index of new reference oil with additives (SAE 5W-30) has a minimum value of 165, while the viscosity index of reference oil without additives (SN90) is 126; for comparison untreated UMO has a viscosity index value of 167. The value of the viscosity index of the oil treated with non-treated bentonite at 120°C for 90 minutes is 229. Optimal results of the viscosity index are UMO treated with bentonite activated with 30% Na_2CO_3 (166), also UMO treated with bentonite activated with 50% H_2SO_4 and 50% $CaCl_2$ and with bentonite activated with 50% H_2SO_4 and 10% Na_2CO_3 at 120°C for 90 minutes, with values of 166 and 168, respectively. The results in Tables 9 and 10 show that the reference oil pour point without additives (SN90) is characterized by maximum value of -26°C, while the untreated UMO pour point is -40°C. UMO treated with bentonite activated with 50% Na_2CO_3 at 120°C for 90 minutes represents the best pour point value (-32). The amount of sulfur present in the reference oil without additives (SN90) is 0.005% (50 ppm), while the amount of sulfur of untreated UMO is 0.186%. The lowest sulfur content UMO samples are those treated with bentonite activated with 10%, 30% and 50% Na_2CO_3 (respectively 0.092%, 0.116%, 0.091%) and with 50% H_2SO_4 and 30% Na_2CO_3 (0.117). By comparing the parameters of UMO (15 000 - 20 000 km), treated with Goshica's bentonite activated with acid(s), alkali(s) and combined method (acids) and alkali(s)), at 90°C for 60 minutes, with the parameters of UMO (15 000 - 20 000 km), treated in the same way but at 120°C for 90 minutes, it can be concluded that Goshica's bentonite activated by the combined method (in the totality of the values of the measurements performed) shows the best efficiency for the UMO (15 000 - 20 000 km) regeneration. This is in full agreement with the activated bentonite parameters; CEC, Ssp, Vt, Smi and Sext, which are the highest in general for the bentonite activated with the combined method.

Conclusions

A used motor oil (UMO) regeneration efficiency was investigated for Goshica's (Kosovo) bentonite with three activation methods; acid, alkaline and combined acid-alkaline activation. The comparison of parameters of UMO (having run about 15000-20000 km) before and after treatment with bentonite activated with acid(s), alkali(s), and by the combined method, were made with the parameters of reference oil without additives of type SN 90 and reference oil with additives of type SAE 5W-30.

The CEC, Ssp, Vt, Smi and Sext were used as key parameters in order to predict the oil regenerating capacity of the bentonite. It turned out that, the higher the CEC, Ssp, Vt, Smi and Sext values are, the better the better the regenerating oil efficiency could be.

In particular, the UMO treated with activated bentonite at 90°C for 60 minutes:

The best density values at 15°C are shown by the bentonite treated oil activated with 10% H_2SO_4, with a value of 0.8424 g/cm^3. Also, the bentonite treated oil activated with 50% H_2SO_4 + 10% Na_2CO_3 with a density value of 0.8474 g/cm^3. The viscosity of new reference oil without additives of type SN 90 compared to the viscosity values of bentonite-treated oil with three activation methods, represents an improvement in viscosity values. The best values are for the bentonite-treated oil with acid activation and the combined method. Good results are presented by the viscosity index of UMO treated with bentonite that has been activated with 30% Na_2CO_3, as well as UMO treated with bentonite that has been activated with 50% H_2SO_4 and 50% $CaCl_2$ and also UMO treated with bentonite that has been activated with 50% H_2SO_4 + 10% Na_2CO_3 at temperature 90°C for 60 minutes.

The UMO treated with activated bentonite at 120°C for 90 minutes:

There is some improvement of the pour point value in UMO treated with 50% Na_2CO_3. Optimal results of the viscosity index are for UMO treated with bentonite activated with 30% Na_2CO_3, also with bentonite activated with 50% H_2SO_4 and 50% $CaCl_2$ as well as bentonite activated with 50% H_2SO_4 and 10% Na_2CO_3 at 120°C for 90 minutes. UMO treated with bentonite activated with 50% Na_2CO_3 at 120°C for 90 minutes represents the best pour point value. The lowest sulfur content UMO samples are those treated with bentonite activated with 10%, 30% and 50% Na_2CO_3 and with 50% H_2SO_4 and 30% Na_2CO_3.

In totality of the values, Goshica's bentonite activated by the combined method shows the best efficiency for the UMO (15 000 - 20 000 km) regeneration, which is in full agreement with the highest values obtained for the activated bentonite parameters; CEC, Ssp, Vt, Smi and Sext.

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