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CONSOLIDATION OF EARTHEN BUILDING MATERIALS: A COMPARATIVE STUDY
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CONSOLIDATION OF EARTHEN BUILDING MATERIALS: A COMPARATIVE STUDY

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Abstract

The consolidation and protection of mud bricks is a challenge in the field of conservation of archaeological sites. One of the solutions is represented by the coverage of the entire excavation that assures a protection against mud dissolution. Unfortunately this is not always feasible, both for economical and practical issues. For these reasons an alternative solution is needed. In this work laboratory experimentation has been carried out in order to test the efficacy of some products to slowdown the dissolution process and increase the brick toughness. Three typologies of raw materials taken from different outcrops (one from the republic of Azerbaijan and two from Calabria region, Italy) have been characterized and used to build mud brick specimens. Four consolidation treatments were tested (ethyl silicate, potassium silicate, potassium hydroxide, sodium hydroxide) and different investigations have been performed to check their efficiency against the dissolution in water. Results suggested that the efficacy of each treatment is related to the main intrinsic characteristics of the raw material employed for the mud bricks manufacture. However, nanolime and NaOH solution showed very poor performance, while ethyl silicate and KOH are very promising compounds for successful conservation.

Keywords

Mud bricks, consolidation, alkaline solutions, laboratory test

1. Introduction

Since ancient times, earth has been the main material used in the construction practice. In some remote and rural areas earthen building continues to be common, despite a shift toward the utilisation of new materials. Examples of earthen architecture are widespread worldwide and several of them are part of the UNESCO World Heritage sites (Houben and Guillard 1994; Amendoeira and Fernandes 2009). The conservation of earthen architecture is always a complex task involving the evaluation of both natural and anthropogenic parameters. Several factors could threaten the earthen building material, among which water take from rainfall, condensation, and capillary rise, are the most important. Various degrees of damage could be produced, ranging from leaks in roofs due to erosion of the mud roof mortars, loss of wall load capacity, deformation of the structures, and macro- and microcracks. Water mainly acts on the clay fraction that constitutes the binder agent for coarser grain size components such as sand and silt. In particular, clay minerals in some cases are affected by expansion and shrinkage phenomena due to humidity changes (Elert et al. 2008). The conservation treatments for earthen structures include different steps, precisely: cleaning and desalination, use of grouts, consolidants, adhesives, and surface coatings (Li et al. 2011). Among these, consolidation is the most widely discussed and studied for non-decorated earthen materials especially in cases of structural decay in archaeological sites. Consolidation effectiveness is related to different parameters such as the physical and chemical compatibility of the consolidants with the substrate, the climate agents (e.g. air pressure, air temperature, precipitation, moisture and solar radiation etc.) and the climate control factors (e.g. latitude, elevation, nearby water, ocean currents, topography, vegetation, and prevailing winds) where consolidation procedure have to be applied together with on site application procedure (Graziani et al. 2015). Therefore, in order to guarantee the durability of original materials and long lasting effect of the consolidants over the distant future, innovative consolidating products have been studied thoroughly and improved in the last 50 years (Mileto et al. 2017). The main objective of this research is the evaluation of the effectiveness of different alkaline solutions as consolidation treatments for raw earth materials, proving their resistance to the harmful action of water. In this regard, three typologies of soil were chosen and experimental mud bricks were prepared. Thereafter solutions such as NaOH and KOH have been applied to identify probable cementing properties provided to the samples and able to decrease the phenomenon of swelling and shrinkage of the clay. In addition, conventional treatments like Ethyl Silicate (TEOS), Potassium Silicate and Nanolime have also been carried out for comparison. Interactions between the components of the raw earth and consolidants were analysed to define the

morphological, mineralogical variations and contribution of the treatments in terms of stability, cohesion and resistance to water of the final consolidated products.

2. Materials and methods

2.1 Provenance of the raw materials and sample preparation

For the experimental analysis, three types of clay-bearing soils with different provenance, genesis, particle size, chemical and mineralogical compositions were chosen. The first one (ID samples AGSU) comes from the archaeological site in the ancient city of Agsu located in the republic of Azerbaijan, in the Caucasus region. This town was built by the founder of the Afshar State, Nader Shah, who came to power in the 1730s, and was the largest city in the Caucasus at that time. A recent archaeological expedition (2010-2012) studied about 1.5 hectare of 40 hectares of the area within the project funded by MIRAS Social Organization on 'Medieval Agsu Town Archaeological Tourism Complex'. The foundation of the fortress walls was constructed of river stones and the walls of raw bricks. A large water canal was laid along the structure for protection purposes. One of the aims of this tourism project included the conservation and restoration of archaeological finds and urban buildings for a better use of the site itself (Fig. 1). The second soil (ID samples KAU) comes from the surroundings of Caulonia (Fig. 2), a historic Greek town along the southeastern (Ionian) coast of Calabria region (southern Italy). The landscape consists of typical *calanchi* (badlands), extremely fascinating hilly landforms dissected by a network of very narrow and steep valleys with a dendritic pattern, separated by sharp, knife-edged ridges (Pulice et al., 2013). The third typology (ID samples ROS) was taken from the coastal river terraces close to Rossano (Robustelli et al., 2009; Scarciglia et al., 2015), a strategic city during the Byzantine Empire, coveted by numerous invaders (Visigoths, Lombards, Saracens), one of the most active and safe in southern Italy, located in the southeastern part of the Sibari plain between the Sila Mountains and the Ionian coast of Calabria (Fig. 2). This region is characterized by a long tradition of using earth as building materials (Cavalcanti and Chimirri 1999, Fratini et al. 2011), from the ancient fortifications of Reggio, dated between the VI and IV centuries B.C. to the more recent constructions, such as in Lamezia Terme, after the catastrophic earthquake of 1783.

The preparation of test pieces for consolidation tests from mixing and moulding is described. Firstly, the bulk soil samples were crushed, ground and selected by means of a 2 mm sieve. The raw earth specimens were created by mixing the soil samples with distilled water. The necessary amount of distilled water was determined by the compaction test consisting of compacting raw earth ideally with a water content which insures its highest density by gravimetric measurements.

After 48 hours from the preparation, the blocks were shaped with dimensions 4x4x4 cm in a plastic grid. The test specimens were left to dry at room temperature for 4 weeks (Fig. 3).

In the first phase of the experiment the following solutions were prepared: 1) NaOH 5 M – 200 g/l, 2) KOH 5 M - 280 g/l, 3) Ethyl Silicate 10% wt (Tetraethylorthosilicate –TEOS-, Estel 1000 CTS, Italy), 4) Potassium Silicate (K_2O_3Si) 10% wt and 5) Nanolime (a suspension of $Ca(OH)_2$ nanoparticles, Nanorestore, CTS, Italy).

Three soil cubes (one for each typology) were placed in airtight containers into which TEOS solution was poured and left under full immersion for 1 hour. Then the solution was taken off and the samples were allowed to stand in open containers to facilitate slow drying (Fig. 4).

At the same time, other cube samples, three for each soil, were placed in plastic bags into which NaOH, KOH and K_2O_3Si solutions were poured until the blocks were totally submerged. The bags were hermetically sealed for 10 minutes. The last cubes of raw earth were treated with nanolime and left to soak for 40 minutes (Fig. 5A). After the preparation, the samples with the NaOH solution underwent a total loss of consistency, while the other ones were placed in dry plastic bags and left to dry at room temperature (Fig. 5B).

2.2 Analytical procedures

The three types of clay-bearing soils firstly powdered and quartered and then were subjected to granulometric analysis, determination of Atterberg limits, X-ray powder diffraction (XRPD), X-ray fluorescence spectrometry (XRFS) and Ionic Chromatography (IC). Moreover, the water resistance and the penetration depth of the various consolidants were evaluated on the treated samples.

For granulometric analysis, the clay-bearing soils were separated into a coarse (particles between 2 and 0.06 mm) and a fine fraction (particles <0.06 mm) in a settling cylinder according to Stokes' law. The fine fraction suspension was further separated into silt (0.06–0.002 mm) and clay (<0.002 mm) via centrifugation at 528 and 2,111 relative centrifugal force (RCF), respectively. The procedure for the determination of Atterberg limits, suitable for evaluating clayey material workability when plastic (Marsigli and Dondi 1997), followed the normative method UNI CEN ISO/TS17892-12 (2005) using a Casagrande apparatus. Mineralogical analysis was carried out through XRPD measurements obtained by a D8 Advance Bruker X-ray diffractometer with Cu Kα radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 0-60°. Measuring conditions were set at 40 kV voltage, 30 mA current, 0.02° 2θ step size, and 3.0 sec step time. Chemical composition of major (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) and trace elements (Ni, Cr, V, La, Ce, Co, Nb, Ba, Y, Sr, Zr, Zn, Rb, Pb) was determined by X-ray fluorescence (XRF) using a Bruker S8 Tiger WD X-ray fluorescence spectrometer, with a rhodium tube (intensity 4 kW

2

intensity and XRF beam of 34 mm). The analysis was carried out on pressed pellets placed over boric acid, using 6 g of specimen (maximum working pressure 25 bar). A Dionex DX 120 equipment on filtered supernatant (filter Minisart RC 25, diameter = 0.45 μm) provided ion chromatography data both on untreated and treated samples, determining ionic species such as SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, Li^+, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}. Finally, water resistance of adobe blocks treated with the different alkaline solutions plus conventional treatments was evaluated by total immersion cycles (2 cycles) in deionized water for 5 minutes, measuring the weight variation of each sample after each cycle. After immersion specimens were dried in an oven at 150 °C for 24 hours, after which the weight was measured.

3. Results

3.1 Grain size analysis and Atterberg limits

Grain size analysis allowed the identification of the percentage of clay, silt, sand, gravel and pebbles of the three examined samples (Table 1). For each sample a granulometric curve was obtained showing the percentages of the constituent grains (Fig. 6).

The fine fraction (silt plus clay) in AGSU and KAU samples prevails over the amount of sand and gravel, while ROS specimen showed the opposite trend. In particular, silt is the largest component in AGSU sample (54%), followed by clay (34%) and sand (12%). Besides, it is interesting to note that the weight percentage of clay and silt particles was fairly similar in KAU sample, 49% and 47% respectively, while it contains only the 4% of sand. On the contrary, ROS sample contains 53% of sand, 21% of gravel, 14% of silt and 12% of clay.

Results obtained after the experimental determination of liquid limit (Wl), plastic limit (Wp) and plasticity index (Ip) are reported in Table 1. As known, the plasticity of fine-grained earths depends on water content, grain-size distribution and composition of clay particles (relative abundance of swelling clay minerals). The lowest plasticity indices recorded for AGSU and ROS samples are related to the predominance of silt and sand respectively. As a consequence, the two soils have shown a low workability. On the contrary, KAU sample, despite having a certain percentage of silt, also contains a fair amount of clay, which determined a good workability (medium plasticity). In addition, this different behaviour in terms of workability could be influenced by the relative abundance of the various clay minerals (Montana et al., 2014). This behaviour could be consistent with the clay mineralogy dominated by non-expandable illite and kaolinite phyllosilicates, with only traces of swelling smectite in the soil samples from Rossano (Scarciglia et al. 2015). A higher amount of pure and interstratified smectite components estimated in the soils from the Caulonia area, although illite, kaolinite and chlorite or vermiculite usually prevailed (Pulice et al. 2013), coupled with a high amount of clay fraction, can explain a higher plasticity than those from Rossano (Pulice 2007).

3.2 Mineralogical and chemical characterization of the untreated soils

XRPD analysis revealed the predominance of quartz in all studied samples, mainly present as sand and silt particles. Calcite was present in remarkable amounts in AGSU and KAU samples while it is absent in ROS sample. Feldspars and clay minerals were subordinate components in all samples. Moreover, traces of hematite have been detected in AGSU specimen, while KAU sample shows the presence of traces of gypsum and strontianite.

The results of XRF analysis performed on whole samples are reported in Table 2. All analysed materials were characterized by a predominance of SiO_2, associated mainly with the presence of quartz, as well as feldspar, micas and clay minerals. Sample ROS showed levels of SiO_2 significantly higher (around 77 wt%). This compositional difference was counterbalanced by a lower amount of calcium oxide (<1%). Al_2O_3, K_2O and Na_2O are comparable in all the samples, while Fe_2O_3 amount is higher in AGSU and KAU (around 7 wt%). This difference could be linked to the higher percentage of silt and clay fractions determined in granulometric analysis. With reference to trace elements, abundances of Ba and Rb can be related to the corresponding volume of K-feldspar and mica, while Sr (geochemically linked to Ca) was abundant in samples KAU and AGSU, both showing high CaO concentrations (21% and 15%, respectively).

3.3 Soluble salts content

Soluble salts content of untreated samples was obtained by IC analysis. The quantitative analyses of ion species are summarised in Table 3. This analysis is important because allows to know the type and quantity of salts content in the samples before the consolidating treatment in order to evaluate the effectiveness of the treatment. In particular, the presence of some soluble salts (sodium sulphate, gypsum, etc.) could determine variations about the penetration and distribution of the consolidating products. All the detected ionic species are compatible with the natural content of non saline soils (Soil Survey Staff 2014). On the contrary, the treatments can determine the formation of new types of salts dangerous for the earthen architecture and building materials.

4. Discussion

3

In the following sections, results after 6 months following the treatment with alkaline solutions and conventional treatments were discussed.

4.1 Mineralogical changes of treated samples

AGSU, KAU and ROS samples treated with KOH experienced the formation of Kalicinite ($KHCO_3$, potassium bicarbonate). This very soluble and hygroscopic salt could seriously damage earthen architecture and building materials in general, especially if specific relative humidity conditions occurred (Greenspan 1977). However, it has been demonstrated that potassium bicarbonate has much lower damage potential if compared with sodium carbonate (Goudie and Viles 1997). On the contrary, ROS sample was the only one that experienced some mineralogical changes after the treatment with Nanolime and NaOH solutions. In particular, the formation of calcite was observed with Nanolime treatment. It constitutes the reaction product of lime and generally improves the resistance of the soil. Regard to the mineralogical modifications after NaOH treatment, the presence of the feldspathoid Cancrinite (a sodium aluminosilicate) was determined. It could be the product of the reaction of sodium alkaline solution with quartz, feldspar and clay minerals.

4.2 Determination of soluble salts of treated samples and SAR index

After the treatment, chromatographic analyses showed, as expected, some changes mainly regarding the concentrations of the Na^+ and K^+ ions (Table 4). To evaluate the impact of the consolidating solutions on soil structures, the Sodium Adsorption Ratio (SAR) (defined as: $Na/\sqrt{(Ca + Mg)/2}$, where concentrations are expressed in $meqL^{-1}$) was defined. This index is among the main parameters to estimate and predict dispersivity (deflocculation) of clay particles in soils (Rengasamy et al. 1984) and has been so far applied especially in badland landscapes (Faulkner et al. 2000; Piccarreta et al. 2006; Pulice et al. 2012). In fact, elevated levels of exchangeable sodium could have adverse impacts on soil structure and cause reductions in water infiltration rates (thus enhancing erosion), decrease aggregate stability, promote clay dispersion, and swelling of expandable clays (Mitchell 1976). SAR index results calculated on untreated and treated samples are reported in Table 5. If the SAR value is higher than 10 the sample is more dispersive, on the contrary if the value is lower, the sample is less prone to clay dispersion. This behaviour is due to the sodium adsorbed in the exchange complex that can cause swelling and/or dispersion phenomena of the clay particles. As seen from the values in the table 6, all treatments, except that with NaOH, provide an acceptable SAR Index (less than 10) assuring no to poor deflocculation to the treated samples. In particular, the AGSU and KAU treated samples with the TEOS have an index even lower than the untreated ones, while Nanolime lowered the SAR value (compared to the untreated) in the ROS sample. Moreover samples treated with NaOH reached elevated values of SAR (> 10) may be affected by an increased dispersivity of clay particles, reduced saturated hydraulic conductivity and aeration, and a general degradation of soil structure. Moreover, the potential damage of salts, which might form during alkaline activation, should be eventually assessed. In fact, as evidenced by mineralogical analyses, the formation of kalicinite occurred. This extremely hygroscopic and soluble salt could be extremely dangerous for the historical earthen architecture.

4.3 Water resistance tests

Data obtained from the water resistance tests were reported in the following graphs (Fig. 7). Results demonstrate how the AGSU soil treated samples with TEOS and KOH have undergone less weight reduction than those treated with Nanolime (Fig. 7A). On the contrary, in the case of KAU sample, there was a significant worsening after all treatments compared to untreated sample (Fig. 7B). In particular after the treatment with TEOS, KAU sample suffered a drastic loss of consistency that led to its almost complete disintegration. ROS soil shows a significant improvement after the treatment with solutions of TEOS, potassium silicate and KOH (Fig. 7C). In general, among the various treatments, potassium silicate and KOH worked better than NaOH, Nanolime and TEOS. Even if mineralogical analysis did not reveal the presence of mineralogical phases with cementing properties (transformation of quartz, feldspar and clay minerals likely have been limited into amorphous phases not detectable by XRD), the water resistance has been improved after some of the used treatments.

4.4 Evaluation of penetration depth

After the consolidation treatment, samples were cut to evaluate the penetration level of the consolidating agent within the specimens. The parameters that influence the penetration process of a capillary fluid are: the viscosity of the fluid itself (in this case of the consolidating product), the diameter of the involved pores and their distribution, and the wetting properties of the material to which the product is applied. A good consolidant must penetrate into the material throughout its structure. A superficial penetration could cause a weight increase of the external layers and their consequent detachment. The untreated specimens were immersed in deionized water for 10 minutes, after that, the depth of penetration was measured. It was determined to be about 2 cm for all the samples. The same procedure was applied to specimens treated with ethyl silicate (TEOS) six months after treatment immersing them in white spirit for 1 h. Figure 8 shows that the product had penetrated the entire block except a small portion in KAU sample.

4

5. Conclusions

Our preliminary results can be considered encouraging to deepen the research on the application of alkaline solutions for the consolidation of mud bricks compared to consolidation methods based on silicates. Mud bricks samples showed a discrete improvement in water resistance especially after treatment with KOH solution that could be the results of the formation of amorphous phases with cementing properties, even if the crystallization of potential damaging soluble salts occurred. Besides, nanolime and NaOH solutions showed very poor performance. Further research will be performed in order to avoid the precipitation of carbonate using for example less concentrated solutions. Clay speciation, particularly the identification of swelling clays, is another aspect that deserves future research. Results of this research, however, show that the application of alkaline solutions for the consolidation of earth structures can be considered a potential alternative to ethyl silicate. Moreover, the acquisition of knowledge about the features of a soil can be considered a strategic step in order to select the suitable conservation materials whose potential performances should be estimated and tested also in situ application.

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Figure captions

Figure captions

Fig. 1 Map location and sampling point of AGSU sample.

Fig. 2 Map location and sampling point of KAU and ROS sample.

Fig. 3 Preparation of test specimens.

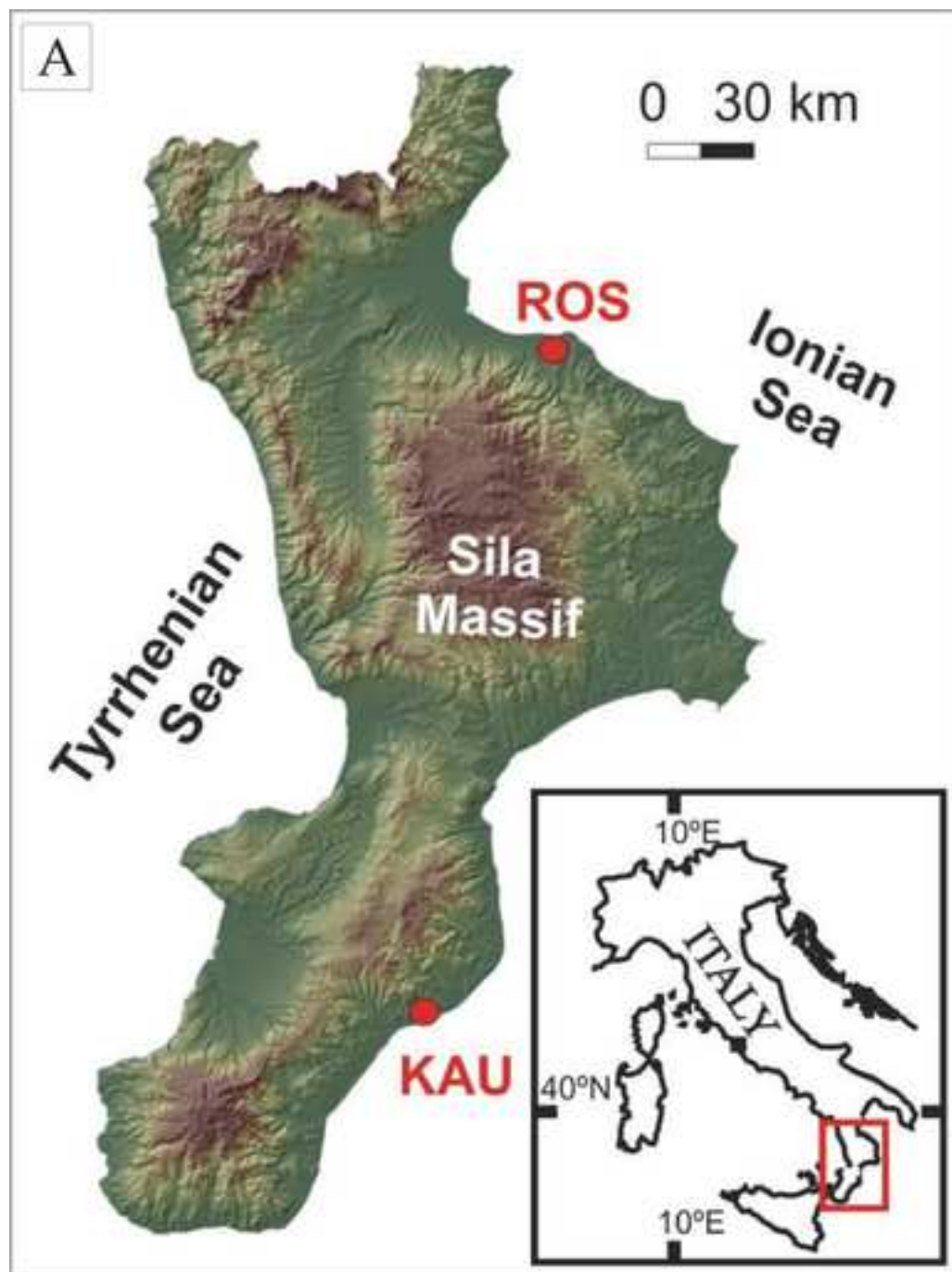**Fig. 4** Treatment of samples with the prepared solutions.

Fig. 5 Loss of consistency of the samples treated with NaOH solution.

Fig. 6 Cumulative grain-size distributions of analysed samples.
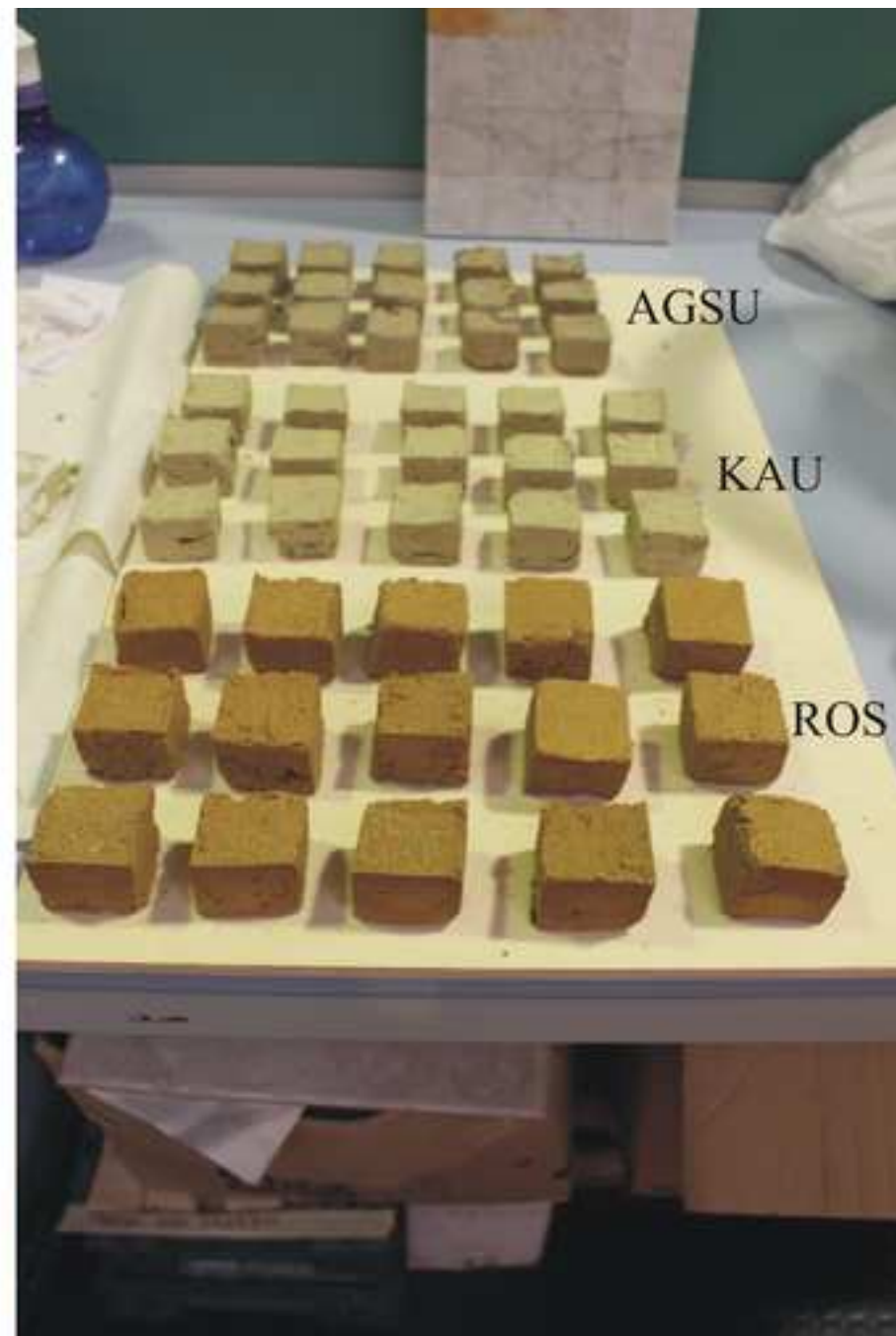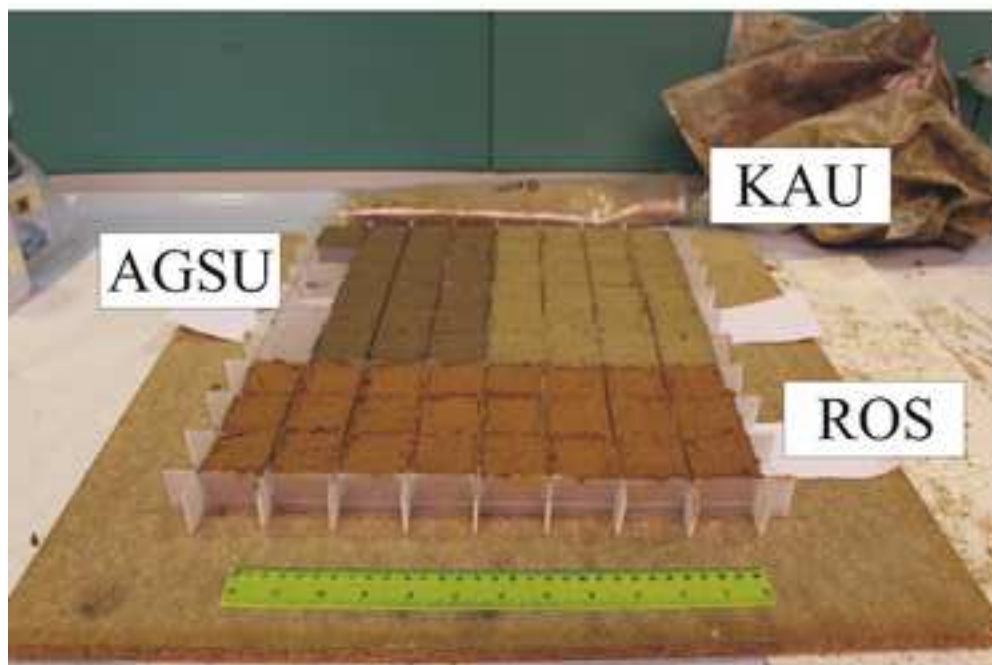
Fig. 7 Results of water resistance test: A) AGSU, B) KAU and C) ROS.

Fig. 8 Penetration depth results: 1. ROS untreated specimen (deionized water immersion); 2. KAU untreated specimen (deionized water immersion); 3. ROS treated with TEOS; 4. KAU treated with TEOS; 5. AGSU treated with TEOS.

Figure 1

Figure 2

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Figure 3

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Figure 4

Figure 5

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Figure 6

Figure 7

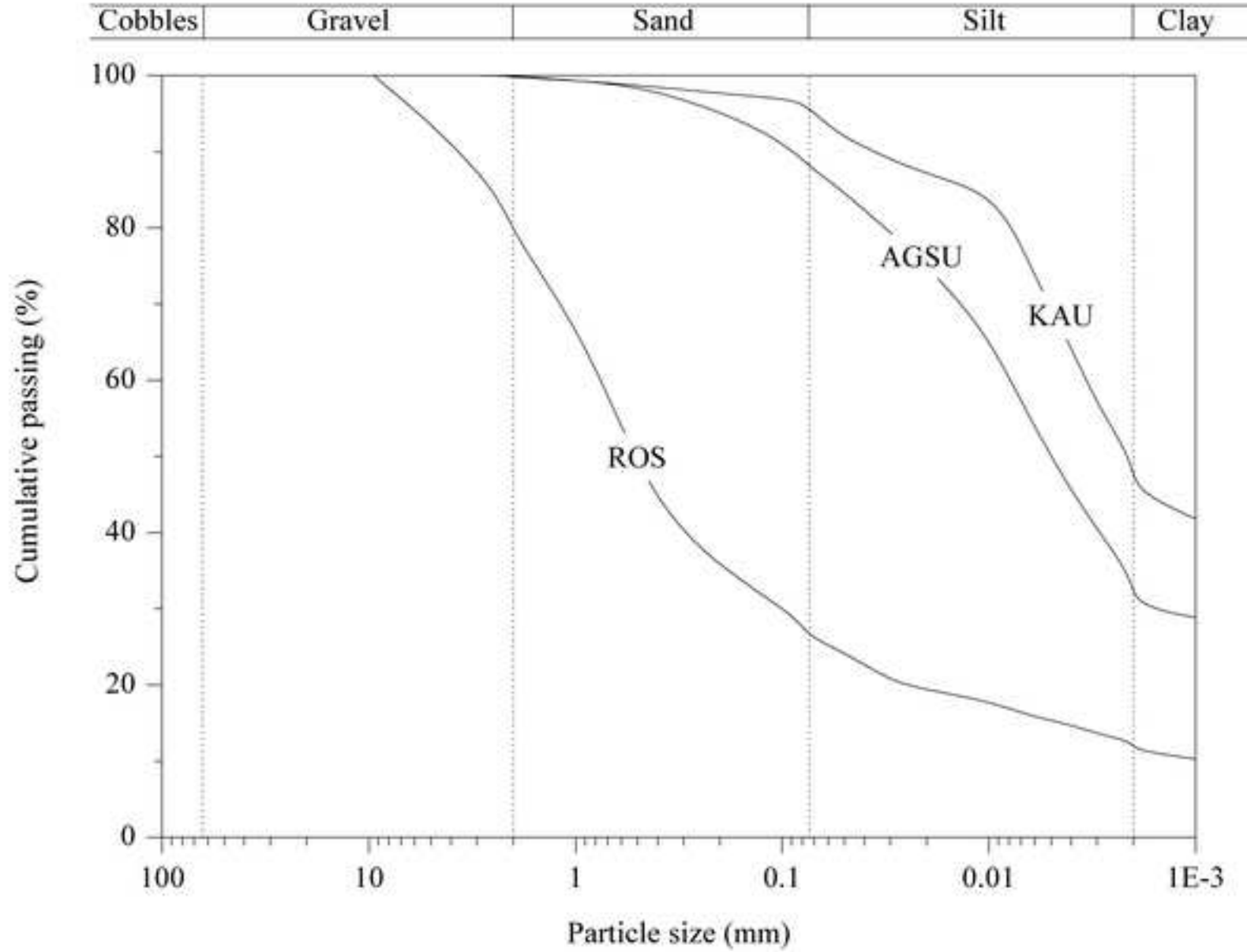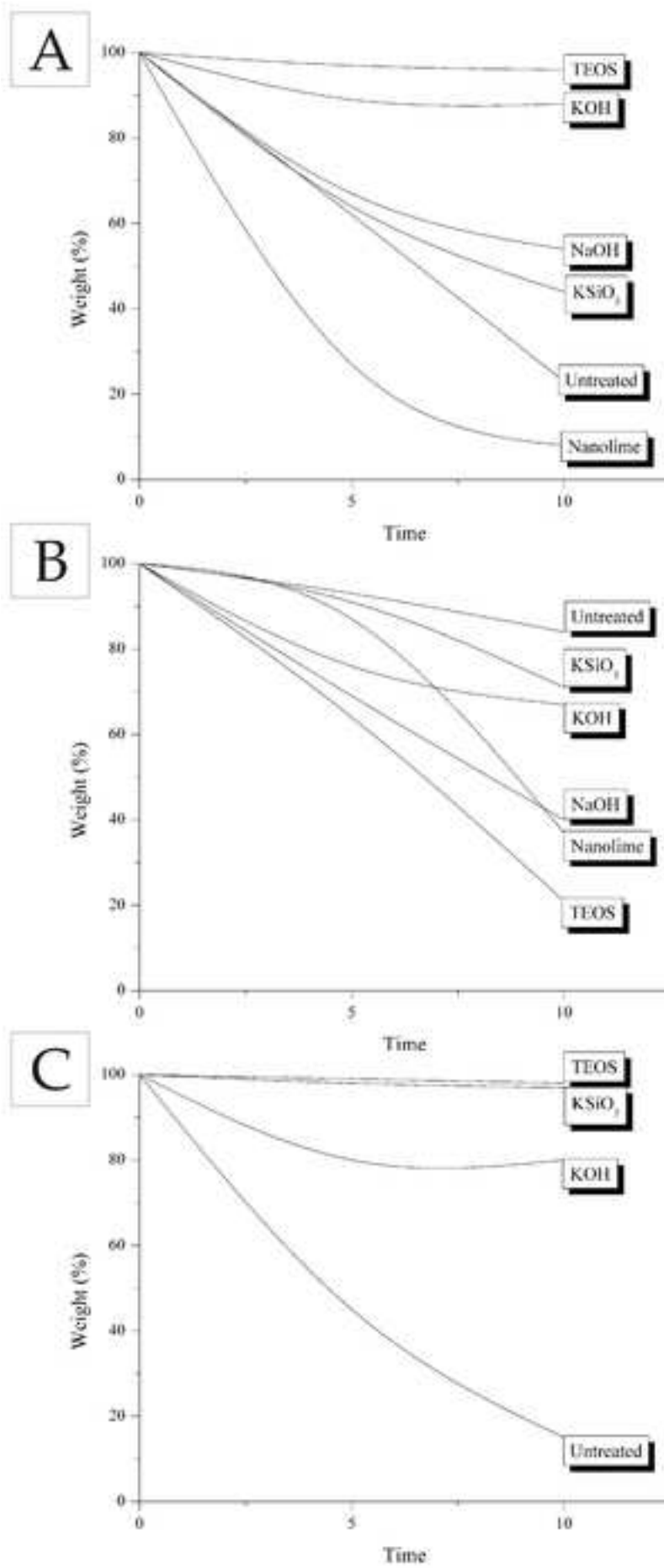Click here to access/download;Figure;Fig. 7.tiff ±

Figure 7

Figure 8
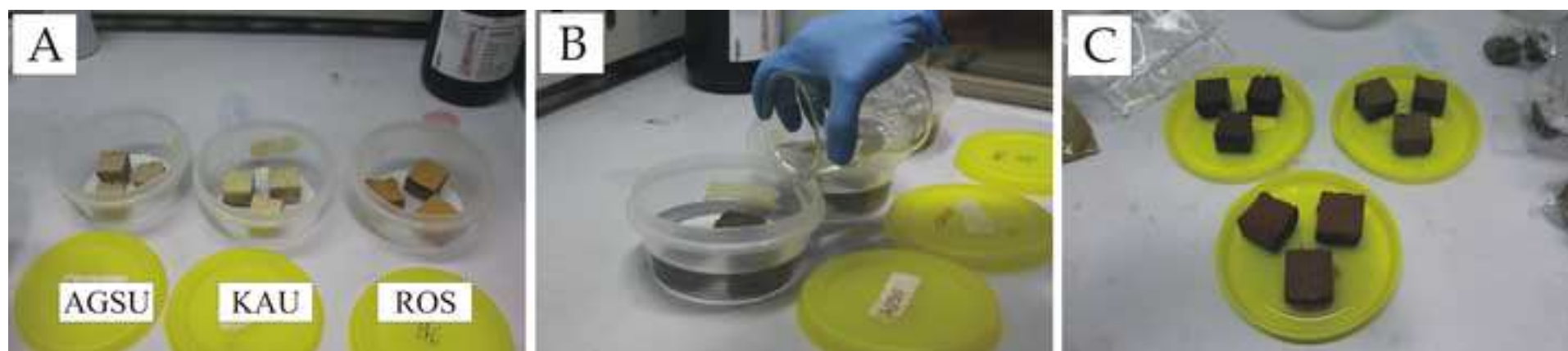
Table captions

Tab.1 Grain-size distributions and Atterberg limits.

Tab. 2 XRF analysis results.

Tab. 3 Ion chromatography analysis of untreated samples.

Tab. 4 Ion chromatography analysis after treatments.

Tab. 5 SAR Index of analysed sample (untreated and treated).

Table 1

	KAU	AGSU	ROS
Gravel (%)	0.18	0.03	20.95
Sand (%)	4.05	11.89	52.70
Silt (%)	46.46	54.25	13.82
Clay (%)	49.31	33.83	12.53
Atterberg Limits			
Wl	50	31	20
Wp	30	28	18
Ip	19	3	1

Table 1.

Table 2

Table 2.

Oxides (%) Elements (ppm)	KAU	AGSU	ROS
Na_2O (%)	0.93	0.84	1.08
MgO (%)	3.96	3.40	1.18
Al_2O_3 (%)	15.00	13.43	13.34
SiO_2 (%)	47.83	55.96	77.33
P_2O_5 (%)	0.16	0.41	0.04
K_2O (%)	2.91	2.96	2.26
CaO (%)	21.00	15.32	0.10
TiO_2 (%)	0.86	0.78	0.51
MnO (%)	0.17	0.17	0.02
Fe_2O_3 (%)	7.18	6.72	4.14
Ni (ppm)	71	56	16
Cr (ppm)	130	93	34
V (ppm)	171	154	68
La (ppm)	21	18	18
Ce (ppm)	68	54	59
Co (ppm)	20	19	9
Ba (ppm)	340	452	372
Nb (ppm)	16	11	15
Y (ppm)	29	29	19
Sr (ppm)	631	466	66
Zr (ppm)	146	162	179
Cu (ppm)	29	45	8
Zn (ppm)	107	123	51
Rb (ppm)	130	101	94
Pb (ppm)	15	23	18

Table 3

Table 3.

Sample code	Li^+	Na^+	NH_4^+	K^+	Mg^{++}	Ca^{++}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
ROS	0.000	0.014	0.000	0.019	0.013	0.021	0.000	0.009	0.000	0.000	0.039
AGSU	0.000	0.011	0.011	0.131	0.033	0.495	0.000	0.010	0.000	0.000	0.087
KAU	0.000	0.252	0.009	0.126	0.039	0.543	0.005	0.040	0.000	0.000	0.561

Table 4

Table 4.

Sample code	Li^+	Na^+	NH_4^+	K^+	Mg^{++}	Ca^{++}	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
ROS KOH	0.000	0.021	0.000	6.578	0.005	0.024	0.000	0.013	0.000	0.000	0.015
ROS Nanolime	0.000	0.014	0.016	0.015	0.029	0.113	0.012	0.013	0.000	0.000	0.025
ROS NaOH	0.000	1.924	0.012	0.007	0.012	0.069	0.009	0.009	0.000	0.000	0.027
ROS K_2O_3Si	0.000	0.035	0.004	1.475	0.010	0.049	0.000	0.006	0.000	0.000	0.019
ROS TEOS	0.000	0.020	0.018	0.028	0.008	0.009	0.000	0.012	0.000	0.000	0.012
AGSU Nanolime	0.000	0.022	0.012	0.109	0.033	0.504	0.013	0.013	0.012	0.000	0.124
AGSU NaOH	0.000	2.071	0.000	0.068	0.008	0.179	0.006	0.010	0.012	0.000	0.084
AGSU K_2O_3Si	0.000	0.037	0.006	1.679	0.010	0.468	0.000	0.006	0.000	0.000	0.094
AGSU TEOS	0.000	0.008	0.015	0.114	0.033	0.697	0.006	0.005	0.012	0.000	0.111
AGSU KOH	0.000	0.020	0.004	7.561	0.011	0.220	0.007	0.008	0.016	0.033	0.136
KAU Nanoclime	0.000	0.257	0.010	0.087	0.045	0.502	0.000	0.044	0.000	0.000	0.572
KAU KOH	0.001	0.312	0.007	7.058	0.028	0.127	0.008	0.040	0.000	0.000	0.355
KAU TEOS	0.000	0.011	0.010	0.115	0.033	0.761	0.000	0.007	0.000	0.000	0.087
KAU K_2O_3Si	0.000	0.267	0.004	2.151	0.011	0.450	0.000	0.030	0.000	0.000	0.332
KAU NaOH	0.000	3.358	0.000	0.035	0.011	0.104	0.005	0.036	0.000	0.000	0.491

Table 5

Table 5.

ROS	SAR	AGSU	SAR	KAU	SAR
Untreated	1.85	Untreated	0.41	Untreated	8.91
KOH	3.12	KOH	1.13	KOH	20.66
NaOH	177.89	NaOH	129.82	NaOH	265.35
Nanolime	0.97	Nanolime	0.80	Nanolime	9.32
K_2O_3Si	3.77	K_2O_3Si	1.48	K_2O_3Si	10.75
TEOS	3.57	TEOS	0.24	TEOS	0.34