PRESERVATION OF CORE INTEGRITY: A COMPARATIVE STUDY OF CORE STABILIZATION PRODUCTS

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This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Halifax, Nova Scotia, Canada, 4-7 October, 2010

ABSTRACT:

In order to perform representative analyses on reservoir-core samples, the core needs to be protected from mechanical and chemical damage before it reaches the laboratory. Various stabilizing products and techniques are used to hold the core intact within the inner-core barrel. The most common stabilization products used in the industry include epoxy resin, polyester resin, expandable foam and Lithotarge. These products are injected into the annulus between the core and the inner wall of the core barrel. Once set, the core is then prevented from moving in relation to the liner during handling and transportation. However concerns have been raised regarding the wettability and permeability preservation when applying these stabilization products.

This paper presents results obtained from laboratory testing of the effect on wettability and permeability resulting from "possible" invasion of these products into the porous rock space. Eight types of sandstones that differ in petrography, porosity (ranging from 18% to 27%), permeability (ranging from 103mD to 2337mD) and wettability have been used in this study. Structural and geochemical analyses have been performed using routine methods. These include petrographical thin sections, Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Environmental Scanning Electron Microscopy (ESEM) and contact angle measurements using a goniometer. Other aspects such as health, environment and safety are briefly discussed. Finally a recommendation for the best non invasive stabilization product that maintains the core integrity is provided.

INTRODUCTION

It has been widely acknowledged that core handling is critical to the maintenance of core integrity. Unfortunately, cores often don't undergo adequate handling procedures to ensure that quality data can be obtained from core measurements [1]. The quality and accuracy of laboratory core analysis depend on the condition of the core material used in the laboratory. Core damage leads to analytical difficulties in the laboratory which can compromise the reliability of core analysis [1] [2]. In order to protect drilled cores from damage during handling and transport from the rig to the core analysis laboratory, it has become a common practice to inject a stabilizing material into the annulus between the core and the core liner. Current stabilization products are resin, expandable foam and Lithotarge. In this study four stabilization products have been tested: polyester resin, epoxy resin, Lithotarge and expandable foam. In order to analyse the effect of the invasion of these products into the porous space, on the rock properties including the wettability, extensive laboratory testing has been performed. These tests include petrographical thin sections analyses, X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), Environmental Scanning Electron Microscopy (ESEM) and contact angle measurements; these tests have been performed on eight sandstone cores that differ in petrography, porosity, permeability and wettability.

ROCK CHARACTERISATION AND SAMPLE PREPARATION

Table 1 shows that the eight rock samples are subdivided into two groups: a group which presents a very high permeability varying between 2020mD and 2337mD, a high porosity varying between 21.5% and 27.5% and a grain density varying between 2.63g/ml and 2.65g/ml. The second group of samples presents a lower permeability varying between 103mD and 118mD, a lower porosity varying between 18.1% and 21.9% and a higher grain density varying between 2.63g/ml and 2.68g/ml.

XRD analysis and the study of the thin sections showed that samples S1 to S4 are poorly to very poorly sorted, present a high porosity and are composed of quartz (10% to 66%), albite (13% to 76%) and K-feldspar (13% to 21%); the clay minerals are less than 1% of the rock (Table 2). Samples S5 to S8 are fine grained sandstones, present a lower porosity comparing to the first group of samples and are composed of quartz (35% to 46%), albite (0% to 10%), K-feldspar (5% to 17%), muscovite/illite (35% to 39%), kaolinite (3% to 6%), ankerite (1% to 2%) and dawsonite (2% for sample S6).

Figure 1 shows the chronology of the different tests performed in this study, an example is given for sample S1. The application of the four stabilization products tested in this study has been performed in the laboratory following as closely as possible the procedure carried out in the field.

EXAMINATION FOR THE PRESENCE OF STABILIZATION PRODUCTS IN THE POROUS SPACE

The examination of the possible invasion of the stabilization products into the porous rock space was carried out using the petrographical thin sections, SEM, XRD and XRF. Table 3 presents the sample selection and stabilization products used in this study.

Visualization of the stabilization and rock interaction

The petrographical thin sections and the SEM technique have been used to investigate the microscale interaction of core samples with stabilization materials. For the SEM analysis, broken surfaces perpendicular to the stabilized-core interface were mounted onto titanium stubs and coated with palladium prior to examination with a Jeol 6310 scanning electron microscope (SEM). Secondary electron images were acquired at an accelerating voltage of 10kV, and X-ray spectra acquired using an Oxford Instruments energy dispersive spectrometer and used qualitatively for mineral and stabilization material identification.

Thin section photos of the eight sandstone samples (P1 to P8) after applying the stabilization products are presented in Figure 2. Representative results of SEM investigation are shown in Figure 3. These photos show that for both Lithotarge and expandable foam minimal infiltration into the pore space was observed. Pores with diameters ranging from 20 to 50µm diameter were observed to be un-invaded by stabilization material, even directly adjacent to the contact (photos A to D of Figures 2 and 3). In sample 7 some 40µm scale kaolinite crystals lining pore space in quartz sand can be seen to be undisturbed within 10µm of the foam lining (photo D of Figure 3).

For both Lithotarge and foam it is clear that as well as the properties of these stabilization products matrices, a key factor in preventing infiltration is the scale of bubbles within the Lithotarge and foam relative to the pore diameter.

Polyester resin that is used for stabilization forms a solid matrix enclosing the outer surface of the sample, and seals grains over a surface topographic range of at least 100µm. This makes removal of the resin from core prior to testing difficult, and results in the outer grains of the core remaining embedded in resin on removal. Examination of pore space at 200-300µm, and at 2-3mm from the resin-core contact also indicates that the resin penetrates deeply into the pore space. Photos G (S2P) and H (S7P) of Figure 2 and photos E (S5P) and F (S3P) of Figure 3 show that polyester resin penetrated the primary interconnected pore space. The samples encased with epoxy resin show that this stabilization product has partially penetrated the pore space; this is probably due to its low viscosity. However this resin covered the quartz, K-feldspar and albite grains (photos G (S1E) and H (S8E) of Figure 3).

Quantification of the content of the stabilization products within the pore space of rock samples

The content of the stabilization products that possibly invaded the pore space of the encased samples is carried out using XRD and XRF. The encased core samples were first cleaned of exterior stabilizing materials using a scalpel, and then hand crushed using an agate pestle and mortar.

For the XRD analysis, the twenty four sandstone samples were analysed for their phase composition using a PANalytical X'Pert Pro X-ray diffractometer. Samples were then mounted as deep well random powder mounts using approximately 2g of sample. These were irradiated using a Cu anode X-ray source operating at 40kV and 40mA, on a spinning stage used to enhance the random orientation of grains. Automatic divergence slits maintain a constant irradiated length of 10mm during a goniometer scan. Scans were acquired from 5 to 70º 2θ, using a step size of 0.008º and a count time of 14.6 seconds per step. A Ni filter was used on the diffracted beam path to reduce any Fe K α fluorescence. Data was presented and analysed using the PANalytical software packages X'Pert data viewer and Highscore plus respectively, in conjunction with the Powder Data File 2008 [3]. Figure 4 shows the diffraction patterns of samples of each of the four stabilization materials used in this study. In each case the undulating pattern with no defined peaks is typical of amorphous materials. Such a pattern should produce a significant, resolvable background in a rock or sedimentary material infiltrated by the casting material in amounts >1% by mass. The minor peaks seen in the patterns for the Lithotarge and expandable foam samples are from the Ni plated steel plug holder. They arise as a result of X-ray penetration through the low density foam materials. Additional peaks in the Lithotarge diffraction patterns are tentatively identified as a result of a Ba-bearing phase. Figure 4 shows representative patterns from samples from a range of sandstone types and with the four different stabilization materials. In each case the pattern for the un-encased core is shown for comparison. Patterns are shown with an enlargement of the 5 to 25º 2θ. For both the expandable foam and Lithotarge the backgrounds are indistinguishable from the un-encased core samples at the resolution of this study. This implies that any infiltration of stabilization material into pore space is at levels below 1 weight % of the total sample mass (Figure 4). Polymer and epoxy resins backgrounds in this range are only slightly elevated relative to un-encased, Lithotarge and expandable foam encased samples. This implies a very slightly higher amorphous material content in samples encased in polymer resin. This may simple be attributable to the fact that whilst both foam based stabilization materials could easily be removed from the sample surface with a scalpel blade, the polymer and epoxy resins could not, leaving a slight residue on the plug surfaces. Where polymer and epoxy resins were broken away from a plug margin it was noticeable that the outer grains from the core remained embedded in resin (diagrams A to C, G to E of Figure 4).

A portable X-Ray Fluorescence spectrophotometer has been used to identify and quantify various elements present in the sandstone rock samples. Each element is identified by its characteristic X-ray emission energy (E). The amount of an element present is quantified by measuring the intensity (I) of its characteristic emission. Count times were 120 seconds in standard (heavy element) mode and 90 seconds on the light element program (LEAP mode). Table 4 shows the X-Ray Fluorescence results performed on the stabilization products Lithotarge and foam. This analysis has not been performed on the resin products because there are not porous components. These results show that foam contains relatively high levels in chloride (Cl), calcium (Ca) and iron (Fe). Other chemical elements such as manganese (Mn), rubidium (Rb) and strontium (Sr) have also been detected. Compared to foam, the Lithotarge contains relatively high K (potassium) and Ca. Table 5 shows the X-Ray Fluorescence results performed on un-encased and encased rock samples. The different chemical components measured on the encased samples are compared to those of the un-encased rock samples in terms of percentage contents (Table 5). This table shows that the stabilized samples with Lithotarge and foam have no chloride (Cl) and the percentages of the other chemical elements vary from 81% to 129%. This shows that foam and Lithotarge have not invaded the pore space. The samples stabilized with the resins epoxy and polyester present lower percentages of the chemical elements varying from 61% to 123%. This is due to the relatively limited invasion of the resin products in the porous space, especially the polyester resin.

WETTABILITY EXAMINATION

Wettability (relative hydrophobic / hydrophilic nature of the mineral phases / reservoir) is an important factor in the prediction of oil or water flow, retention and likely oil yield. The wettability characteristics of a porous medium play a major role in various measurements including: capillary pressure, relative permeability, electrical conductivity, waterflood recovery efficiency and residual oil saturation [4]. In this study, two techniques have been used to observe the dynamics of wetting and any change in wettability of the different rock samples: the ESEM (environmental scanning election microscopy) using a Quanta 3D FEG ESEM and the contact angle goniometry using an OCA 15 plus, which is a video based optical contact angle measuring device. Using a syringe delivery system, a sessile water drop is placed on the surface of rock samples; the measurement of contact angles between the water droplet and mineral phase allows the determination of hydrophobicity / hydrophilicity of minerals through digital image capture and analysis software. Figure 5 shows images of contact angles for sandstone samples S3, S4, S5 and S6 before and after applying the stabilization products and Table 6 shows the measured contact angles. Figure 6 presents ESEM photos showing the wettability property of the sandstone samples S1, S2, S7 and S8 before and after applying the stabilization products. This study showed that the two techniques (ESEM and contact angle measurements) show similar results; samples S1, S3, S6 and S7 are water wet (contact angle < 90^o), samples S2 and S5 have an intermediate wetness (contact angle ~$90\ ^o$) and samples S4 and S8 are oil wet (contact angle > 90^o). The ESEM and the contact angle measurements showed that the stabilization products Lithotarge and foam have not altered the wettability properties of the sandstone samples (S1L, S3L, S4L, S5L, S6L, S8L, S2F, S4F, S6F, and S7F). The samples encased in epoxy resin are oil wet (S1E and S8E); the resin epoxy has altered the wettability of sample S1. Polyester resin has not altered the wettability of the stabilized samples, which present a wettability property varying from extreme water wet to intermediate wetness (S2P, S3P, S5P and S7P). Some chemicals in the resins may have the ability to alter wettability [3]. The latter has consequences for Special Core Analysis (SCAL) such as relative permeabilities, capillary pressures and electrical properties that often are performed on “preserved” or “native state” samples. Consequently, this might mean that samples for special core analysis should not be stabilized with resin based products.

DISCUSSION

Several qualitative and quantitative measurements have been made to study possible invasion of stabilization products (foam, Lithotarge, epoxy resin and polyester resin) into the pore space of two groups of sandstone samples that differ in mineralogy, petrophysical and wettability properties. The results of the different methods used were found to be consistent with each other. The petrographical thin sections and the SEM images showed that both Lithotarge and expandable foam exhibit minimal infiltration into the pore space of the samples; this is most probably due to the size of bubbles which are greater than the pore diameters. Epoxy resin partially penetrated the pore space and polyester resin penetrated into the pore space deeply. Both XRD and XRF analyses supported these findings i.e. foam and Lithotarge have not invaded the pore space while the epoxy and polyester resin showed an invasion into the porous space, especially the polyester resin. This might be attributed to the fact that whilst foam based stabilization materials could easily be removed from the sample surface with a scalpel blade, the polymer and epoxy resins could not, leaving a slight residue on the sample surface. The ESEM and the contact angle measurements showed that the stabilization products Lithotarge and foam do not alter the wettability properties of the sandstone samples. The samples encased with epoxy resin are oil wet while polyester resin has not altered the wettability of the un-encased samples, which were extreme water wet to intermediate wet. It would be interesting to check the possible wettability change of an originally oil wet sample before stabilizing with epoxy.

The stabilization products tested in this study contain isocyanates or Polyol as the main component. Exposure to Lithotarge and foam during the actual stabilization procedure of the core is minimal. The use of these two stabilization products involves the utilization of self contained pressurised canister and does not require any mixing of any of the components it contain. In addition the cured Lithotarge and foam are classified as general waste and after use the cylinders should be properly disposed according to certified waste management practices. Unlike Lithotarge and foam, resins require a premixing because they are usually composed of two-component systems in order to control the hardening time. This is an intrinsically hazardous operation and requires measures to be taken to ensure that health and environmental hazards do not occur. In addition the use of resins involves using various items such as mixers, hosepipes and jugs which should be properly disposed. Moreover, practice learns that a pump to inject the resin is rarely used because of the inherent complexity of cleaning and maintenance after use.

CONCLUSIONS

In this study we investigated the effect of possible invasion of stabilization products on rock properties and the interaction of these products with rock. Several observations have been made during this study:

- Both expandable foam and Lithotarge preserve core integrity and when carefully removed provide core that is suitable for porosity and permeability determination.
- Lithotarge and foam perfectly seal to the core surface and do not affect wettability.
- Resins effectively impregnate cores and preserve the textural condition allowing petrographic study and image analysis.
- Resins alter the wettability of the stabilized rock.
- Epoxy resin exhibits qualities that are less favourable than foam and Lithotarge but better than polyester resin.
- Lithotarge and foam have lower weight compared to resins, are simpler to process and have technical and environmental advantages over resins. They can easily be peeled off from the core surface. This helps to determine the slabbing orientation and allows immediate access to the core for geological description.
- Lithotarge and foam are the best products for core stabilization.

ACKNOWLEDGEMENT

The authors wish to thank Dr Ken P’Ng from the Centre for Material Research, Queen Mary University of London for the ESEM measurements.

REFERENCES

1. Hjelmeland, O., Tjetland, B.G., Bolle, L., Schele, A., Venturini, C. A new method for stabilization of friable and unconsolidated core samples at well-site, International Symposium of the Society of Core Analysts, 1996, paper 9603.
2. Skopec, R.A., Collee, P. and Tyler, P. Recent advances in coring technology: new techniques to enhance reservoir evaluation and improve coring economics, International Symposium of the Society of Core Analysts, Montpellier, France, September 8-10, 2006.
3. Chung, F. H. (1974) Quantitative interpretation of X-ray diffraction, I. Matrix-flushing method of quantitative multicomponent analysis, J. Appl. Cryst, 7, 513-519.
4. Baraka-Lokmane, S., Main, I., Ngwenya, B. and Elphick, S. (2009) Application of Complementary Methods for More Robust Characterization of Sandstone Cores, Marine and Petroleum Geology, 26, 39-56.

Table 1: Petrophysical parameters of the eight groups of samples

Sample	He Porosity, Φ (%)	Gas permeability, k_g (mD)	Grain density, ρ (g/ml)
S1	27.50	2105	2.63
S2	22.40	2337	2.64
S3	24.00	2020	2.64
S4	21.50	2261	2.65
S5	19.20	103	2.63
S6	19.80	106	2.67
S7	21.90	112	2.67
S8	18.10	118	2.68

Table 2: Mineralogy composition of the eight groups of samples (from 3-D XRD analysis)

Sample	Key minerals (%)						
	Quartz	Albite	K-feldspar	Muscovite/illite	Kaolinite	Ankerite	Dawsonite
S1	10	76	13	0	0	0	0
S2	58	26	16	0	0	0	0
S3	49	29	19	0	3	0	0
S4	66	13	21	0	0	0	0
S5	35	4	17	39	6	0	0
S6	42	0	13	38	4	1	2
S7	46	10	5	35	4	0	0
S8	44	8	5	38	3	2	0

Table 3: Sample selection and stabilization products used in this study

Casting material	Sample							
	S1	S2	S3	S4	S5	S6	S7	S8
Polyester resin		S2P	S3P		S5P		S7P	
Lithotarge	S1L		S3L	S4L	S5L	S6L		S8L
Foam		S2F		S4F		S6F	S7F	
Epoxy resin	S1E							S8E

Table 4: X-Ray Fluorescence results of Lithotarge and foam (from 3-D XRF analysis)

Stabilization product	Cl (ppm)	K (ppm)	Ca (ppm)	Mn (ppm)	Fe (ppm)	Rb (ppm)	Sr (ppm)
Lithotarge	28890	2580	11271	78	350	4	40
Foam	74363	0	1304	133	786	7	35

Table 5: X-Ray Fluorescence results of the uncased and cased samples (from 3-D XRF analysis)

Sample	K (ppm)	Content (%)	Ca (ppm)	Content (%)	Mn (ppm)	Content (%)	Fe (ppm)	Content (%)	Rb (ppm)	Content (%)	Sr (ppm)	Content (%)
S1	23944		3823		53		2507		65		586	
S1- L	22062	92	3874	101	58	109	2504	100	65	100	599	102
S1-E-R	18692	78	3383	88	65	123	2149	86	63	97	568	97
S2	19936		2518		69		2846		52		403	
S2-F	20076	101	2551	101	72	104	2361	83	60	115	459	114
S2-P-R	17714	89	2450	97	69	100	1991	70	57	110	435	108
S3	18641		2408		49		1128		50		421	
S3-L	18938	102	2874	119	53	108	1281	114	54	108	442	105
S3-P-R	13694	73	1477	61	47	96	869	77	41	82	328	78
S4	18487		1681		38		1189		44		324	
S4-L	22413	121	1689	100	37	97	1392	117	45	102	418	129
S4-F	19148	104	1767	105	41	108	1256	106	42	95	334	103
S5	14903		1878		101		6767		77		112	
S5-L	13834	93	1548	82	90	89	6723	99	83	108	119	106
S5-P-R	14223	95	1489	79	96	95	7302	108	80	104	116	104
S6	13965		10135		415		5992		63		89	
S6-L	13638	98	10766	106	432	104	6326	106	66	105	97	109
S6-F	13450	96	9874	97	409	99	5774	96	62	98	94	106
S7	17192		3638		151		5882		84		154	
S7-F	15086	88	2956	81	127	84	5234	89	78	93	141	92
S7-P-R	14612	85	2830	78	119	79	4581	78	84	100	146	95
S8	14150		17784		812		7359		63		99	
S8-E-R	12738	90	16191	91	710	87	5752	78	67	106	99	100
S8-L	14014	99	15753	89	705	87	6632	90	63	100	99	100

Table 6: Measured contact angles using the contact angle goniometer

Sample	Right contact angle	Left contact angle	Average	Wettability
S1	54	64	59	Water wet
S1- L	56	64	60	Water wet
S1-E	139	153	146	Oil wet
S2	88	104	96	Intermediate wetness
S2-F	96	98	97	Intermediate wetness
S2-P	53	67	60	Water wet
S3	51	67	59	Water wet
S3-L	51	55	53	Water wet
S3-P	42	54	48	Water wet
S4	113	121	117	Oil wet
S4-L	109	121	115	Oil wet
S4-F	102	110	106	Oil wet
S5	88	90	89	Intermediate wetness
S5-L	84	98	91	Intermediate wetness
S5-P	84	100	92	Intermediate wetness
S6	47	57	52	Water wet
S6-L	74	82	78	Water wet
S6-F	61	75	68	Water wet
S7	18	22	20	Very Water wet
S7-F	17	29	23	Very Water wet
S7-P	20	28	24	Very Water wet
S8	98	106	102	Oil wet
S8-E	97	111	104	Oil wet
S8-L	155	159	157	Oil wet

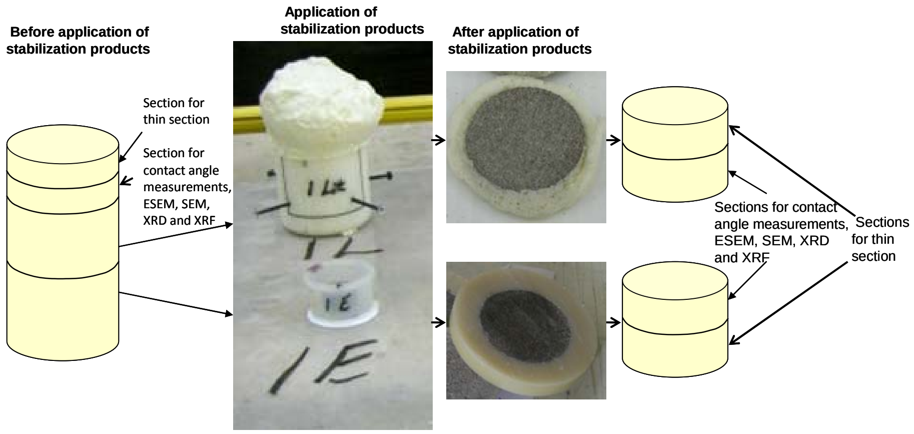

Figure 1: Diagram showing the chronology of the tests performed in this study, example of sample 1

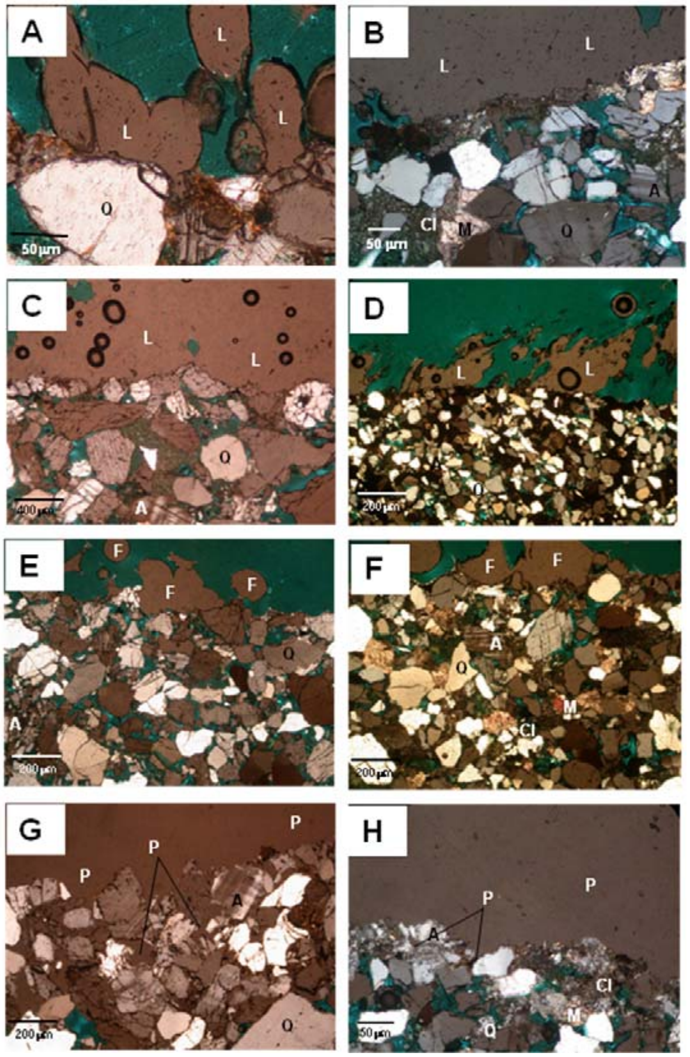

Figure 2: Thin section photos of the eight group of samples after applying the stabilization products (Q: quartz, K-F: potassium feldspar, A: albite, Cl: clay, M: mica, L: Lithotarge,
F: foam, P: polyester resin, A: S1L, B: S8L, C: S3L, D: S5L, E: S4F, F: S6F, G: S2P, H: S7P)

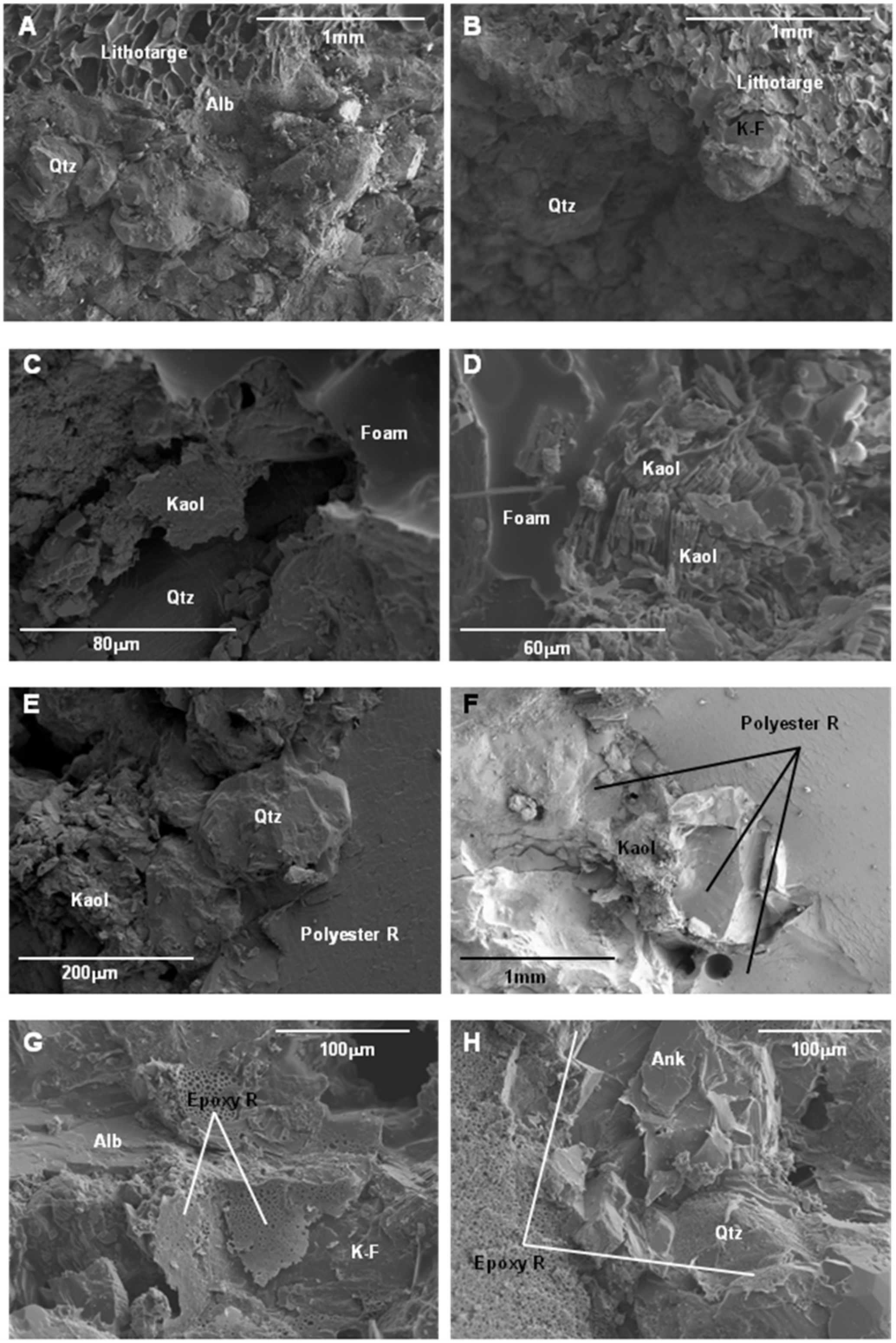

Figure 3: Representative views of the cased core samples with the four stabilization products (Q: quartz, K-F: potassium feldspar, Alb: albite, kaol: kaolinite, Ank: ankerite, L: Lithotarge, F: foam, P: polyester resin, A: S4L, B: S6L, C: S2F, D: S7F, E: S4P, F: S3P, G: S1E, H: S8E)

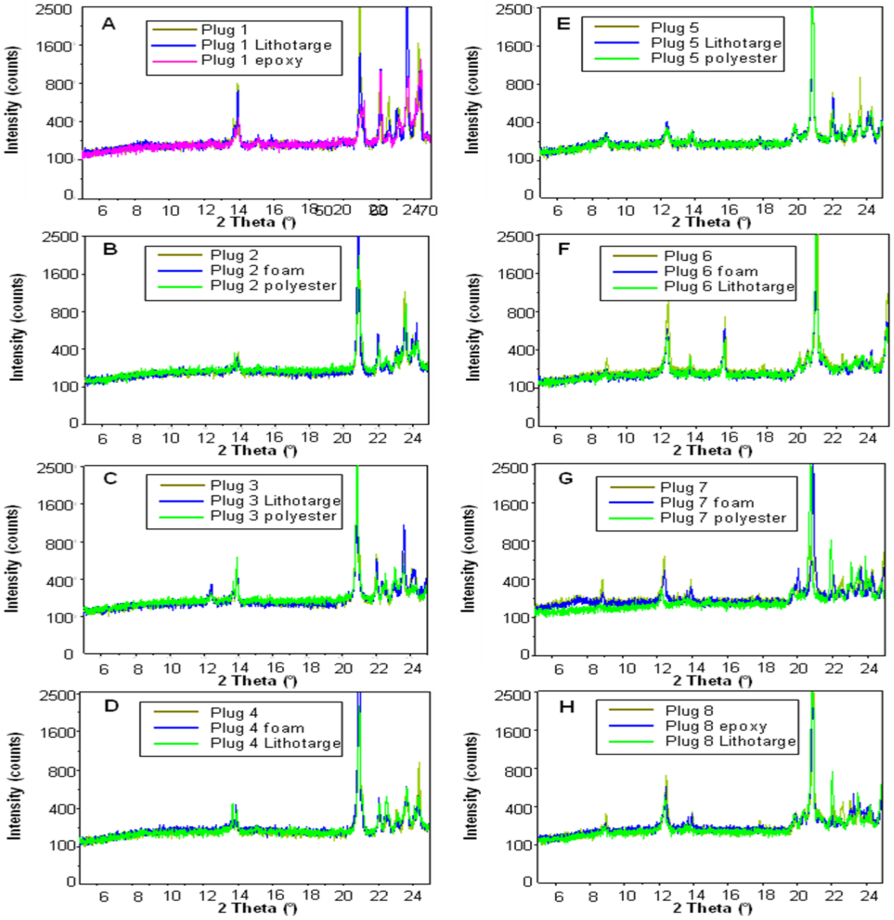

Figure 4: Representative X-ray diffraction patterns for a range of eight sandstone types with different casing materials

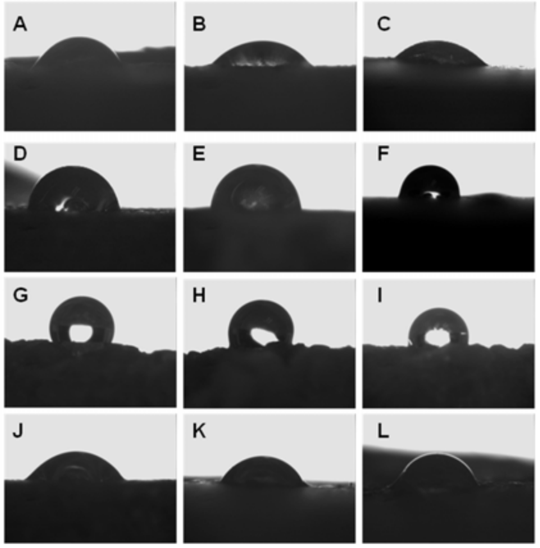

Figure 5: Contact angle Goniometer photos showing the wettability property of the sandstone samples before and after applying the stabilization products (A: S3, B: S3L, C: S3P, D: S5, E: S5L, F: S5P, G: S4, H: S4L, I: S4F, J: S6, K: S6L and L: S6F)

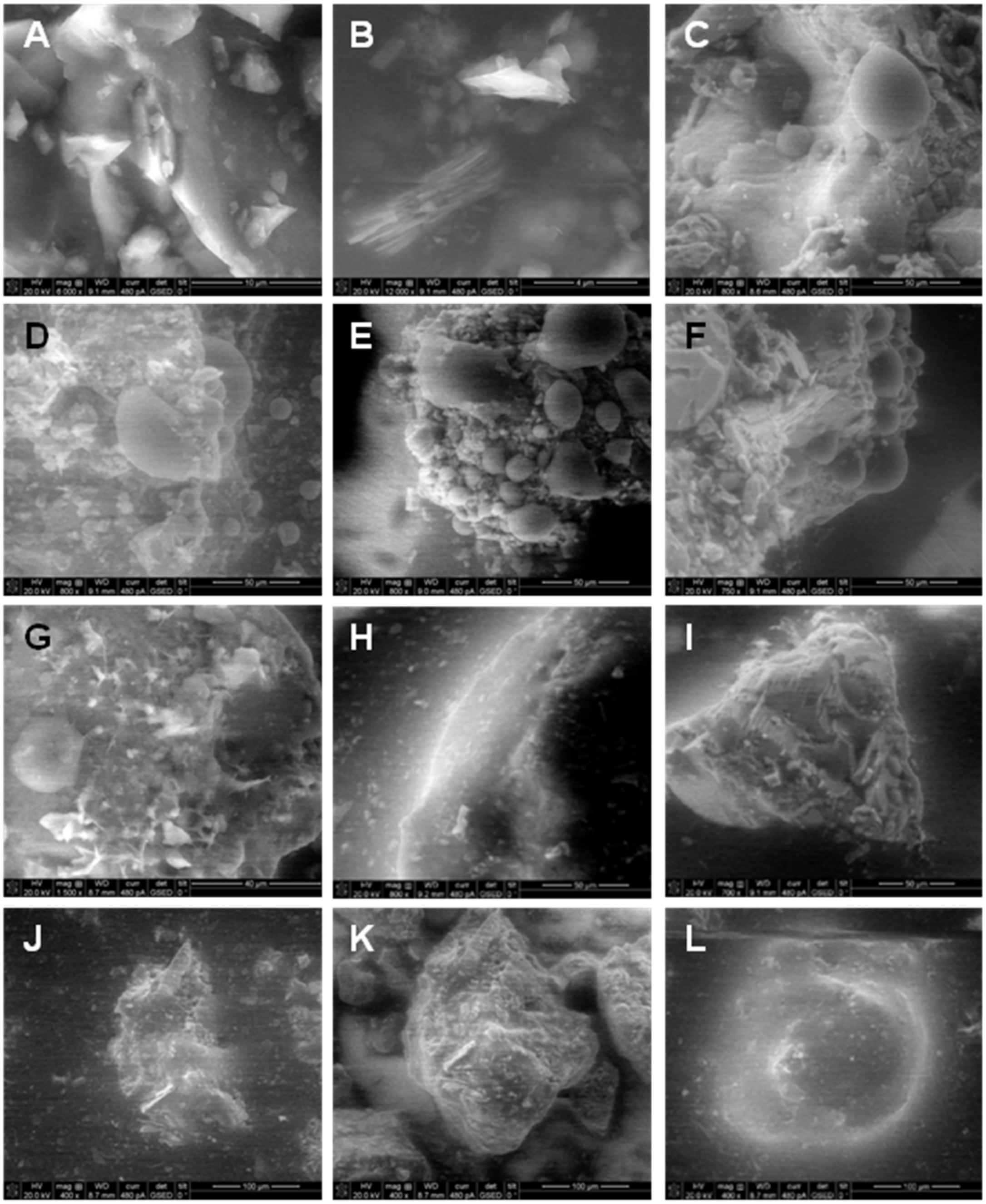

Figure 6: ESEM (Environmental Scanning Election Microscope) photos showing the wettability property of the sandstone samples before and after applying the stabilization products (A: S1, B: S1L, C: S1E, D: S8, E: S8L, F: S8E, G: S2, H: S2F, I: S2P, J: S7, K: S7F and L: S7P)