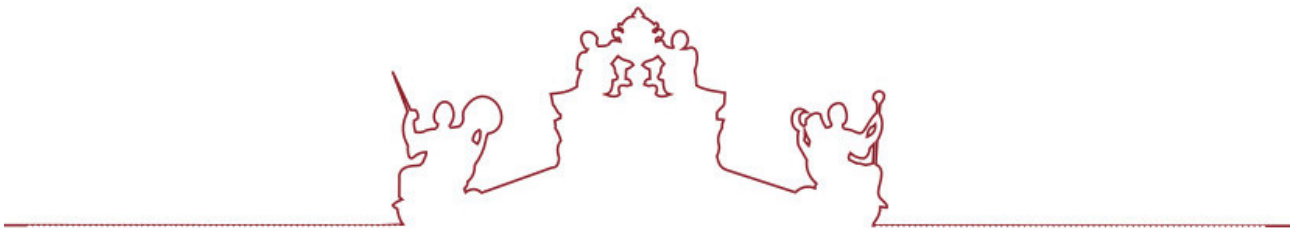

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Università degli Studi di Roma "La Sapienza" Aristotle University of Thessaloniki

Mestrado em Ciência dos Materiais Arqueológicos (ARCHMAT)

Dissertação

The Study of Edvard Munch Sketches Collection in View of It's Conservative Treatment

Madhavan Calapatti Suresh

Orientador(es) | Pedro Miguel Barrulas
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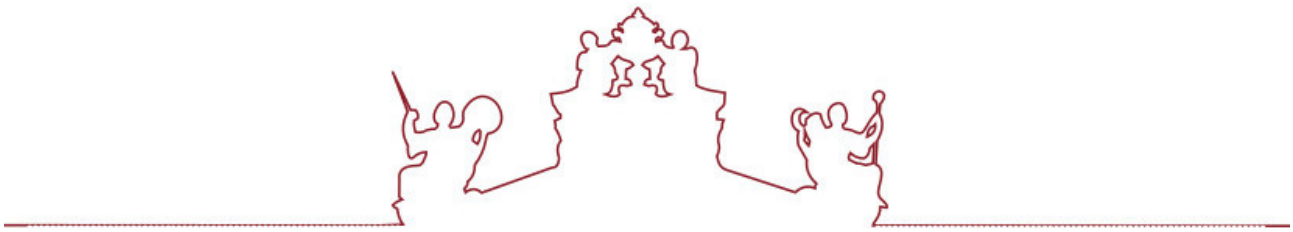

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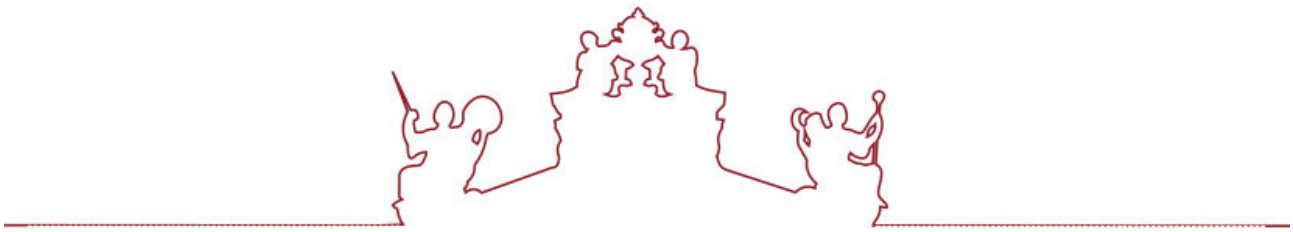

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UNIVERSITY OF ÉVORA

ARCHMAT

ERASMUS MUNDUS MASTER IN ARCHaeological MATerials Science

"The Study of Edvard Munch Sketches Collection in View of it's Conservative Treatment"

MADHAVAN CALAPATTI SURESH, 48238

Évora, Portugal, November 2022

ARISTOTLE UNIVERSITY OF THESSALONIKI

UNIVERSIDADE DE ÉVORA

SAPIENZA UNIVERSITÀ DI ROMA

ABSTRACT

“The Study of Edvard Munch Sketches Collection in View of it’s Conservative Treatment”

Edvard Munch (1863–1944), a Norwegian painter, was one of the most renowned artists of the19th and 20th century. Munch produced great artworks where among them in the “Scream”, one of the most famous paintings in the world. In 1914 Edvard Munch was commissioned to decorate the new assembly hall at the University of Oslo. Munch’s paintings in the University Aula have become a major work within Norwegian monumental painting. Edvard Munch had used fifteen large canvases as sketches for the Aula Magna paintings. These canvases were stored by being exposed to extreme outside environmental conditions and now they present salt efflorescences on their surface and are in dire need of conservation. Therefore, it is the main goal of the present thesis to find novel solutions / products in order to remove and/or stabilize these salts. For this purpose, mock-ups that imitate the structure and composition of Munch’s sketches were created and artificially aged to create salts on their surface (mainly calcium and magnesium sulfates). And for the cleaning solutions / products, agarose and polyacrylamide gels (both plain and loaded gels with various cleaning solutions) were created. These gels were then systematically tested on the mock-ups at multiple time steps in order to determine their efficiency in the removal of salts. FT-IR-ATR, XRD and SEM-EDS were used to characterize the mock-ups, the salts and the sample mock-ups after various gel treatments. Laboratory analyses provided new insights into the ‘cleaning’ capabilities of various agarose and polyacrylamide tested gels.

Keywords: Edvard Munch; salt efflorescences; FT-IR-ATR, XRD, SEM-EDS, Agarose gels; Polyacrylamide gels

RESUMO

“Estudo da colecção de esboços de Edvard Munch com vista ao seu tratamento de conservação”

Edvard Munch (1863–1944), pintor Norueguês, foi um dos artistas mais conceituados nos séculos XIX e XX. Munch produziu grandes obras de arte, entre as quais o “grito”, uma das pinturas mais famosas do mundo. Em 1914, Edvard Munch foi contratado para decorar o novo salão de reuniões da Universidade de Oslo. As pinturas de Munch da Aula da Universidade tornaram-se numa das obras mais importantes da pintura monumental norueguesa. Edvard Munch utilizou quinze telas de grandes dimensões para o esboço das pinturas da Aula Magna. Estas telas foram armazenadas sendo expostas a condições ambientais extremas e agora apresentam eflorescências salinas na sua superfície e precisam urgentemente de tratamento de conservação. Assim, esta dissertação tem como objetivo principal encontrar novas soluções/produtos para a remoção e/ou estabilização destes sais. Para tal, foram criados provetes com estrutura e composição similares aos dos esboços de Munch e estes foram envelhecidos artificialmente para fazer cristalizar sais na sua superfície (principalmente sulfatos de cálcio e magnésio). Para as soluções/produtos de limpeza, foram criados géis de agarose e poliacrilamida (géis simples e carregados com várias soluções de limpeza). Esses géis foram testados sistematicamente nos provetes criados para o efeito, com vários tempos de aplicação, para determinar a sua eficiência na remoção destes sais. FT-IR-ATR, XRD e SEM-EDS foram as técnicas utilizadas para caracterização dos provetes, dos sais e dos provetes após vários tempos de aplicação dos géis. As análises laboratoriais permitiram introduzir novos conhecimentos sobre as capacidades de "limpeza" de vários géis testados de agarose e poliacrilamida e respetivas formulções.

Palavras-chave: Edvard Munch; Eflorescência de sais; Géis de Agarose; Géis de Poliacrilamida

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CHAPTER 1

INTRODUCTION

"I was walking down the road with two friends when the sun set; suddenly, the sky turned as red as blood. I stopped and leaned against the fence, feeling unspeakably tired. Tongues of fire and blood stretched over the bluish black fjord. My friends went on walking, while I lagged behind, shivering with fear. Then I heard the enormous, infinite scream of nature." (Faerna, 1995).

1.1. THE SCREAM project…

'TOUCHSTONE FOR HERITAGE ENDANGERED BY SALT CRYSTALLIZATION: A RESEARCH ENTERPRISE ON THE ART OF MUNCH'

Funded by FCT in Portugal.

Project Ref:

(2018-2022; FCT-ALT20-03-0145-FEDER-031577)

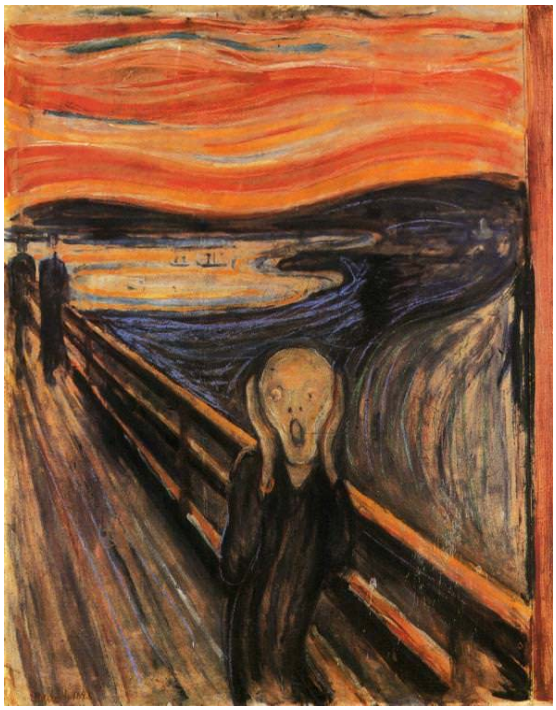


Fig. 1.1. The Scream by Edvard Munch (www.EdvardMunch.org).

The research project that allowed the development of this Master's thesis is a scientific collaboration between the HERCULES Laboratory at the University of Évora and the Munch Museum in Oslo, aiming to study several sketches on canvas

from the museums' collection where efflorescences were found to be formed and the utmost need to be removed (Cardoso *et al.*, 2019).

Munch used fifteen large canvases as preparatory drawings for the Aula Magna paintings (see fig. 1.2) of the Oslo University. These canvases were stored, exposed to the outside environmental conditions and further stored and handled in inappropriate fashion resulting in extensive fold marks, deformations, tears, holes, degraded fibres, mould, stains, and tide lines and several of them have severe amounts of salts' efflorescence visible on their surfaces (Sandbakken *et. al.* 2012).

Fig 1.2. The Aula, University of Oslo. (UiO/Terje Heiestad 2013).

Thus, *THE SCREAM* project aims at; the scientific and technical study of Edvard Munch canvases (which present salt efflorescence) present in the Munch Museum in Oslo. The identification of the salts which is crucial to mitigating their

effects on the canvases. And the removal of these salts which are necessary in order to create optimal conservation conditions.

1.2. Aims and Objectives…

Seeing as how the Edvard Munch's Aula magna preparatory sketches were stored in less-than-ideal conditions and how detrimental the development of salt efflorescences on their surface can be. There is an utmost need for conservative intervention. Thus, the present thesis is aimed at;

A. Obtaining of mock-ups imitating the structure and composition of the sketches and their artificial ageing, mimicking the weathering cycles to which the real objects were subject to.
B. Characterization of the crystals which are formed during the accelerated ageing.
C. Creation of theoretical models for the de/re-crystallization processes and predictive environmental model.
D. Development of novel formulations for treatments to be applied for the removal or stabilization of the salts.

A multi-analytical methodology will be adopted in order to fulfil these aims and objectives.

1.3. A brief on Edvard Munch and the Aula Magna Paintings…

Fig. 1.3. Edvard Munch self-portrait with a cigarette, Oslo, National gallery (Høstland, 2011).

Edvard Munch was born on December 12th, 1863, in Löten, Norway. He was a Norwegian painter who was most notable for his work 'The Scream' (see fig. 1.1), a painting which has been associated with the onset of modernism in both art and society. Munch led an emotionally challenged life and would often try to portray his emotions in his art. His hardships would start right from his childhood when at the age of 5 he would lose his mother to tuberculosis as well as his sister in 1877 (Eggum, 1984; Wolff, 1989). Then he would be raised by his father (Christian

Munch) and his aunt (Karen) who also tutored him. About his father Munch wrote "My father was temperamentally nervous and obsessively religious to the point of psychoneurosis. From him I inherited the seeds of madness. The angels of fear, sorrow, and death stood by my side since the day I was born". Christian reprimanded his children by telling them that their mother was looking down from heaven and grieving over their misbehaviour. According to Munch this morbid pietism from his father negated his positive behaviour towards his children. Often ill and so out of school he would draw to keep himself occupied (Prideaux, 2005). Edvard Munch himself felt that death was constantly hounding him and would write that "I inherited two of mankind's most frightful enemies-the heritage of consumption and insanity" (Eggum, 1984). No doubt these thoughts were spurred on by the oppressive and religious and death ridden environment he was born into.

Owing to his father's low-income, Munch would move constantly from one cheap flat to another and thus, most of his early art would depict these interiors and objects like medicine bottles and drawing implements. And by his teen's art would be the dominating interest in Munch's life (Eggum, 1984). Quite early in his life Munch was influenced by impressionists such as Édouard Manet and later on by post-impressionism artists like Vincent van Gogh and Paul Gauguin (edvard-munch.org). He dabbled in many styles including naturalism and impressionism. Munch would later come into a relationship with Hans Jæger (the local nihlist) who lived by the code "a passion to destroy is also a creative passion" and who advocated suicide as the ultimate way to freedom. Munch stated that "My ideas developed under the influence of the bohemians or rather under Hans Jæger. Many people have mistakenly claimed that my ideas were formed under the influence of Strindberg and the Germans… but that is wrong. They had been formed by then" (Prideaux, 2005). Under Jæger's commandment that Munch should "write his life", Munch set out to

explore his own emotional and psychological state, he began a period of reflection and self-examination, recording his thoughts in his "soul's diary". Here he had decided that impressionism did not allow for sufficient expression and felt a need to explore deeper into emotional and expressive content (Prideaux, 2005).

Later in 1889 Munch would present most of his works till then which would get him a two-year scholarship to study in Paris under Léon Bonnat (french painter). Here he would learn from Paul Gauguin, Vincent van Gogh and Henri de Toulouse-Lautrec. In Berlin, he embarked on a major series of paintings he would later call The Frieze of Life, and in 1893 in Kristiania (later renamed Oslo), he would go on to conceive ‘the scream’.

In 1914 Munch was commissioned to decorate the Aula and he would finish this work in 1916. Totalling to 11 paintings *The sun*, *history* and *Alma Mater* (see fig. 1.4 – 1.6) being key-works it is considered as a major work in Norwegian monumental paintings. Much declared “I wanted the decorations to form a complete and independent world of ideas, and I wanted their visual expression to be both distinctively Norwegian and universally human" (University of Oslo, 2014).

Fig. 1.4. *The Sun*, by Edvard Munch, University of Oslo (www.EdvardMunch.org).

Fig. 1.5. *Historien*, by Edvard Munch, University of Oslo (Woll, 2009).

Fig. 1.6. *Alma Mater*, 1911, by Edvard Munch, University of Oslo (www.EdvardMunch.org).

Munch died on 23rd January, 1944, after which the city of Oslo inherited the remainder of his works for which a museum (Munch Museum) was built at Tøyen that opened to the public in 1963.

1.4. Previous Work…

More than 130 sketches that Edvard Munch produced between 1909-1916 for the decoration of the Aula Magna (University of Oslo) now reside with the Munch Museum (Cardoso *et al*, 2019). One of these sketches *Alma Mater / The Researchers* (see fig. 1.7) has previously been analysed by the National Museum in Denmark with results concerning the use of pigments, oils, binders and consolidants in this sketch (Singer *et. al.*, 2010).

Fig. 1.7. *Alma Mater/The Researchers,* 1910, Edvard Munch, Munchmuseet (https://www.munchmuseet.no/en/object/MM.M.00906).

Munch painted and stored many of the sketches outdoors (for four years) and 31 of them have been stored on rolls. Many of these sketches now show extensive salt efflorescence, most likely as a function of exposure to extreme outdoor elements such as rain, low temperature, snow, sun radiation etc. (Sandbakken *et. al.*, 2012).

24 samples *"6 fibre fragments, 6 drawing materials, paint layers and white efflorescence from differently coloured areas"* were chosen for preliminary analysis.

The material characterization was carried out at the HERCULES Laboratory (as part of THE SCREAM project in collaboration with the Munch Museum in Oslo) using micro-X-ray diffraction (μXRD), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS) and micro-Fourier Transform Infrared Spectroscopy (μFTIR) (Cardoso *et al.*, 2019).

"The preliminary results show the presence of sulphates namely magnesium sulphate hexahydrate ($MgSO_4 \cdot 6H_2O$), magnesium sulphate heptahydrate ($MgSO_4 \cdot 7H_2O$) and hydrous sulphate of sodium and calcium $Na_2Ca(SO_4)_2 \cdot 4H_2O$" (Cardoso *et al.*, 2019).

1.5. Current Cleaning Methods in Conservation…

Various materials and methods are commonly used by conservators for the surface cleaning of paintings. These procedures are generally referred to as 'dry cleaning', among which the most common are PVC-based erasers (also known vinyl erasers), powder gums, mouldable materials, sponges and microfibre clothes (Daudin-Schotte, *et. al.*, 2013). The PVC-based erasers demonstrate a permanence of chemical residues (plasticizers) after surface treatment, the sponges and mouldable materials present excessive stickiness and potential polishing action on the treated surface. While the sponges base on polyurethane ether or styrene-butadiene rubber, are generally safe to use after a preliminary rinsing with water to remove harmful additives and antioxidants (Cremonesi, 2016).

However, some surfaces and soiling materials might require the use of aqueous based solutions. While these solutions may be very efficient against the soiling materials, they may have many detrimental effects towards the treated surface itself; loss of pigment can occur as a result of the weaking of the pigment-

to-medium bond especially in water sensitive paint media such as acrylic emulsion paints. The leaching of water-soluble components (surfactants), blanching of paint and varnish layers and the deposition of harmful cleaning agents and other residues may also occur among other things. Much of the problems occur mainly for the simple reason that aqueous based solution rarely penetrates only one layer, they go deep into the surface through any gaps, cracks and capillaries, from there they weaken, swell, distort and even destroy any water sensitive material present in the treated object (Carlyle, 2016).

Further, the commonly used mode of application of these aqueous solutions are cotton swabs, cotton rolls or brushes of various sorts which result in a high level of interaction with the surface that undergoes excessive mechanical stress caused by the weakening, swelling and distortion caused by the aqueous solutions. They may also cause raising and ripping of fibres on canvases or paper which can also lead to delamination (Iannuccelli & Sotgiu, 2010).

Thus, when aqueous solution-based treatment is necessary but traditional methods do not afford enough control over said aqueous solution and when there is concern over the water sensitivity of the treated object, there is a need for an alternative treatment method with more control. This is where aqueous cleaning solutions in gels seem to show good promise.

1.6. Gels in conservation…

Agar (also known as agar-agar), is a mixture of galactan derivatives extracted from certain red seaweeds, and agarose is *"that mixture of agar molecules with the lowest charge content and, therefore, the greatest gelling ability, fractioned from a whole complex of molecules called agar, all differing in the extent of masking with*

charged groups." (Renn, 1984; Duckworth *et. al.*, 1971). Agarose is a rigid polysaccharide consisting of an alternating copolymer of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose residues (fig. 1.8) (Araki, 1956). It can be used as an aqueous gel which has shown great promise as a poulticing material (a porous solid that can be filled with a solvent used for cleaning) and as a solvent gel. And owing to its porous nature the agar gel can act as a molecular sponge, solubilizing impurities, lifting them from the surface and holding them within the gel matrix (Scott, 2012). Also, the great advantage of rigid gels is that they can deliver water (or other aqueous solutions loaded prior into the gel) in a very controlled manner (through a process known as syneresis) whilst generally not requiring any posttreatment rinsing (Cremonesi, 2013).

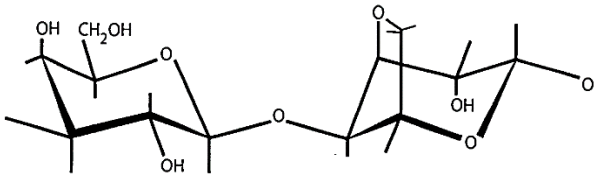


Fig. 1.8 Agarose repeat unit (Warda, 2007).

The process of gelation of agarose involves a shift from a random coil in solution to a double helix in the initial stages of gelation and then to bundles of double helices in the final stage (Cambrex) (see fig. 1.9). This process is quite easy to undertake in the real world as agarose is readily soluble in water above 85 °C and once the solution is cooled below 37-39 °C the polymer molecules tightly assemble into a regular mesh of double helices forming a rigid gel (Cremonesi, 2017).

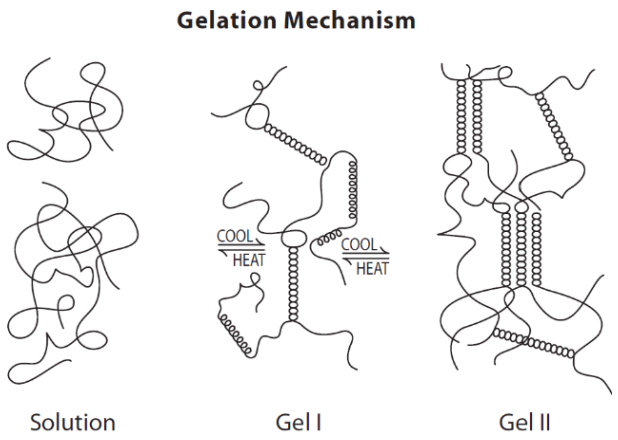


Fig. 1.9. The various molecular stages of the gelation process of agarose (Cambrex).

"Agarose has received limited attention in the conservation literature as a poultice material. While it is often used in combination with enzymes (Pell 1990; Dyke 2003; Bowen 2004), it has also been used alone (O'Loughlin and Stiber 1994) in the removal of moisture-sensitive adhesives from paper. Pell (1990) credits Wolbers for developing the former technique in 1983. In addition, agarose was proposed in combination with bleaching agents for local bleaching of paper (Burgess 1988)" (Warda, 2007). In the early 2000s, the use of rigid agar gels for application on painted surfaces was introduced by Richard Wolbers (2000) which showed great promise and in later years the scope was broadened to include wooden objects, plaster sculptures and mural paintings (Campani *et. al.*, 2007; Anzani *et. al.*, 2008). The rigid gels, besides its use for cleaning of painted surfaces, can also be used for structural interventions in the form of removal of adhesives and consolidants. The use of gels in conservation, specifically agar or agarose has gained a lot attention for cleaning treatments over the past few years mostly by Italian conservation scientists Marilena Anzani and Paulo Cremonesi (Scott, 2012).

An agarose gel need not be used simply by itself, rather a gel can be loaded with an aqueous solution of diluted and weak acids or bases, chelating agents, surfactants, or alcohols to create a targeted approach to specific materials (such as resins, oils, waxes, and salts). Further, the gels have a very wide range of application time, where, they can either be applied on the intended object for only a few minutes (where only a minimal release of cleaning solution is necessary) or for a much longer period of time until the gel completely dries out in cases where deep penetration is required or for salt removal. These treatments have been deemed safe for artwork as many analytical studies have shown that only trace amounts of polysaccharides are left behind on the treated objects (Cremonesi, 2017). However, these treatments and materials have still not been adapted perfectly to the conservation field yet and creating novel solutions to enhance the cleaning performance of these materials remains a challenge.

Polyacrylamides are water-soluble synthetic linear polymers made of acrylamide and acrylic acid with the general chemical formula (-$CH_2CHCONH_2$-). Polyacrylamide gels form by the co-polymerization of acrylamide and a cross-linking agent which is usually bis-acrylamide (N,N´-methylene-bis-acrylamide). The polymerization is furthered by the production of free radicals which involves the use of ammonium peroxodisulphate (APS) and tetramethylene ethylenediamine (TEMED). Here, the APS acts as a free radical generator and the TEMED which is the catalyst, accelerates this production. Propagation reactions occur wherein the polymer chains elongate and are randomly crosslinked (see fig. 1.10). The resulting gel acts like a sieve or a sponge with a controllable pore size just like an agarose gel. The tuning of the density and consistency is achieved by changing the monomer/cross-linker ratios (Cambrex; Baglioni, 2012).

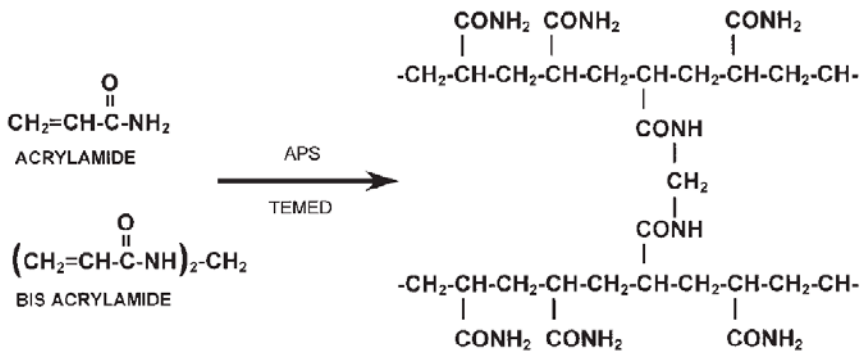


Fig. 1.10. Polyacrylamide gel polymerization (Cambrex).

Polyacrylamide gel electrophoresis (PAGE) has become a popular technique to separate proteins and nucleic acids because of its high resolution, ease of use and flexibility (Cambrex). The gel's chain network consists of covalent bonds, which provides stronger cohesion forces in terms of "physical" gels or viscous crosslinked polymer solutions, this makes the gels very suitable for cleaning procedures, since they do not leave residues upon application and their hydrophilicity allows for them to be loaded with cleaning solutions (Baglioni, 2012). And same as the agarose gels the loaded polyacrylamide gels diffuse the solutions therein, in a controlled manner further making them ideal for conservation purposes.

The tuneable consistency, easy handling and good retention of water and aqueous cleaning solutions exhibited by both agarose and polyacrylamide gels make them efficient in cleaning canvas, wood, paper, among others, thus making them very compelling tools in the arsenal of a conservator.

CHAPTER 2

MATERIALS AND METHODOLOGY

2.1. Materials Used…

2.1.1. Sample Mock-ups…

Mock-ups imitating the structure and composition to that of Edvard Munch's sketches for experimentational purposes were created by priming cotton canvases with dolomitic lime and casein before artificially accelerating the ageing and formation of salts (the process of making has been detailed later on).

For this purpose, 1m of pure unbleached cotton was acquired from a local (Evora, Portugal) textile shop. Dolomitic lime (https://www.microlime.pt/en/products/#dolomiticlime) was also acquired, and 200g of casein (a fine powder derived from water-soluble lactic acid often used as a binder in combination with other materials) was bought from a reputable online shop (http://www.restaurarconservar.com).

2.1.2. Gels and Solutions…

Agarose and polyacrylamide gels were chosen as the media for testing the removal of the salts. Polyacrylamide gels were prepared using acrylamide (99.9% purity, Electran®, VWR chemicals), bis-acrylamide (Ultra-pure grade, AMRESCO®), ammonium peroxodisulphate (APS) (>98% purity, AnalaR NORMAPUR®, VWR chemicals) and lastly tetramethyl ethylenediamine (TEMED) (≥ 99 % assay, Sigma-Aldrich, Merck chemicals). Both the gels were also

loaded separately with butanol, isopropanol and acetone, and tested independently for their efficiency in treating the salts.

Lastly, two generic food grade silicone moulds (one flat-bottomed and the other round-bottomed) were purchased for use in the setting and ease-of-removal of the gel(s).

2.2. Instrumentation and Experimental Conditions…

Instruments that aided in the preparation of the mock-ups and the gels (agarose and polyacrylamide) were; a grinder, heating magnetic stirrer, a desiccator, high-precision weighing scales and a microwave (generic).

Instruments that were used for analytical purposes were; FT-IR-ATR, HIROX digital microscope, X-Ray Diffraction and SEM-EDS instruments. Note that all the analytical techniques used are non-invasive and non-destructive.

The complete details and precise experimental conditions of all the relevant instruments have been expounded below.

Grinder...

The ‘Planetary Ball Mill PM 100’ by Retsch® ‘Milling Sieving Assisting’ was used to grind the dolomitic lime (0.2mm grain size) to an extra fine powder. Operational settings used: 3 steel balls in 20mL jar, @500Rpm for the time duration of 30min. (https://www.retsch.com/products/milling/ball-mills/planetary-ball-mill-pm-100/function-features/)

Heating Magnetic Stirrer…

AREX Hot Plate Stirrer with CerALTop™ by VELP® SCIENTIFICA was used to create a homogenous solution of dolomitic lime, casein and water. Operational settings used: no heat applied, @1000Rpm, for time duration of ~43min (https://www.velp.com/en-ww/arex-ceraltop-hot-plate-stirrer.aspx).

Fourier Transform-Infrared – Attenuated Total Reflectance (FT-IR-ATR).…

Bruker© A250/D ALPHA FT-IR with Platinum-ATR modular attachment in support with the OPUS 6.5 software was used to carry out material characterization of the mock-ups. Operational settings used: Number of ATR reflections – 1, ATR angle of incidence – 45°, Mean reflection index of sample – 1.5, Material of ATR crystal – Diamond.

Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS).…

The HITACHI S-3700N Variable Pressure – Scanning Electron Microscope (VP-SEM) was used for both (high resolution and high magnification images) of the surface of the mock-ups, to determine the presence of salts (and their types) and to also determine the efficiency of the gel treated areas of the samples. And the EDS (Bruker XFlash® Detector 630M) was used (in support) with the ESPRIT Compact software for elemental analysis to determine with absolute certainty the presence/lack of salts (their types), the extension of their spread and again the efficacy of the gel treated areas. Operational settings used: accelerating voltage – 20KeV, chamber air pressure – 40Pa in variable pressure mode, sample holder –

15x14mm multi-holder (the large size of which allowed the loading of two samples at once) (https://cleanroom.gatech.edu/articles/2096).

HIROX Digital Microscope…

The HRX-01 HIROX flagship digital microscope was used to obtain high resolution/magnification images, 3D mapping images as well as topographic images. The HRX-01 is equipped with a 5MP sensor (for 4K resolution with HDR) and with motorized HR lenses. Operational settings used: Lenses – 20-140x (Wide-range), 140-1000x (Mid-range), 700-5000x (HR-5000E, High-range) lenses at 0° inclination to the normal, HDR – on, resolution: 4K, top lighting system – 80% and above intensity, Software: HIROX 4K Interface.

(https://hirox-europe.com/products/3d-digital-microscope/hrx-01-new-3d-digital-microscope/).

X-Ray Diffraction (XRD)…

The Bruker D8 DISCOVER X-Ray Diffractometer coupled with the LYNXEYE (1D mode) linear detector was used to characterize the material composition of the samples. Operational settings used: Tube – Cu tube with 1.5418 [Å], @ 40kV & 40mA, Scan type – Coupled 2Theta/Theta, Scan mode – continuous PSD fast, Time / Step – 1 (1438 total steps), 2Theta – 3.0001°-74.9971 / Theta – 1.5001°-37.4986°. Software used for analysis and identification respectively: DIFFRAC.SUITE EVA and ICDD PDF-2 database. (https://www.bruker.com/en/products-and-solutions/diffractometers-and-scattering-systems/x-ray-diffractometers/d8-discover-family/d8-discover.html)

2.3. Methodology…

2.3.1. Preparation of Mock-ups…

The first step in the preparation of the mock-ups was creating stretched canvas samples (of which 30 total examples were made). This was achieved by stretching small pieces of locally sourced cotton (pure and unbleached) over and between 2 stout plastic cylinders (improvised) of roughly 3cm diameter which generally seemed to work quite well as it fit quite snug and held constant and consistent pressure over the canvas for the duration of the thesis (see fig. 2.1).

Fig. 2.1. Top view of all 30 canvases stretched over/between plastic holders.

Preparation of a dolomitic casein solution was carried out to be applied as a thin coat/layer on the prepared canvas samples which would serve as a base for the salt formation and subsequent treatment efforts.

The dolomitic lime with a grain size of 0.2mm was too coarse for quick dissolution and thus it was ground down to a very fine powder using the grinder (planetary ball mill) at 500rpm operating for 30min (see fig. 2.2). This yielded a satisfactory fineness of powder to continue with the making of the dolomitic casein solution. The casein powder was already fine enough and did not need further grinding.

Several attempts were made in order to find the most suitable and effective procedure for dolomitic casein solution preparation.

Fig. 2.2. Dolomitic lime ground to a very fine powder.

Dolomitic casein solution was prepared through dissolution of 4.83g of dolomitic lime in 20mL of distilled water and in order to avoid the casein from lumping again, a heating magnetic stirrer was employed to keep the solution in constant spin at 1000rpm with no applied heat. Then ~0.5g of casein was added to the solution every 3 - 3 ½ min until the solution was homogenous with no lumps which took 43min on the stirrer and consumed 7.36g of casein.

The resulting dolomitic casein solution was then applied to all the necessary canvas samples (30 in total) via a generic painter's brush and left to dry (naturally out of sunlight) for 2 days. This yielded the desired outcome of a canvas sample with a thin base coat of dolomitic casein solution (now dried) ready for salt formation.

2.3.2. Salt Formation…

The process of artificially inducing salt formation was done via a desiccator with an SO_2 atmosphere. Thus, 29 prepared canvas samples were chosen of the total 30 available (1 sample left out as control for later analytical measurement prior to the induction of salt formation). They were seated in the desiccator (no desiccant was used) before being sealed air tight (see fig. 2.3). Then, a sufficient quantity of pure sulphur dioxide gas (SO_2) (99% pure, SO_2.N30 B5 Air Liquide) was introduced into the chamber via a valve at the top before being stored away (not under any special conditions, except for out of direct sunlight) for 17 days. After which time the chamber was aired for the first time (in open air for safety reasons) and the samples (now with salts on the surface confirmed later on after analysis, detailed later on) promptly retrieved.

Fig. 2.3. The desiccator chamber along with the samples just after the SO_2 was introduced.

In this way the mock-ups necessary to carry out experimentation of various treatment options for the removal and or mitigation of the salts were created.

2.4. Agarose Gels…

2.4.1. General method of Preparation…

The general method of creating an agarose gel involves mixing an amount of agarose in an amount of water, applying heat till the solution reaches >85°C which homogenates the solution and letting it cool to <39-37°C which sets the solution into a gel. The percentage of the agarose gel depends on the ratio of quantities between the agarose and the water (example: 10g of agarose in 100mL of water yields a 10% agarose sol./gel).

The process of creating an agarose gel ‘loaded’ with a cleaning solvent involves the addition of the said cleaning solution to the homogenous agarose and water solution (after being heated to over 85°) before thoroughly mixing the solution and letting the solution to cool and gel.

Much of the technique used to create agarose gels (both loaded and unloaded) in the present thesis were adopted from the method prescribed by Cremonesi and his team (Cremonesi, 2017). This method involves using a standard microwave as the heat source to boil the agarose and water solution and letting it fully gel before re-boiling it and letting the solution gel again. This ‘double boiling' technique allows for a clearer/transparent gel.

2.4.2. Unloaded/plain Agarose Gel…

A 4% unloaded/plain agarose gel was obtained using the above mentioned double boiling method. The solution was poured out into 5 glass petri dishes (see fig. 2.4) and let rest for an hour which was sufficient enough for the solution to gel. However, the choice of a glass petri dish to set the gel proved counterproductive as none of the gels were released from the dish without extensive breakage. Therefore, silicone cookie moulds were used to set the rest of the gels (both agarose and polyacrylamide) which proved to be quite successful as their flexibility allowed for a much smoother release of the gels.

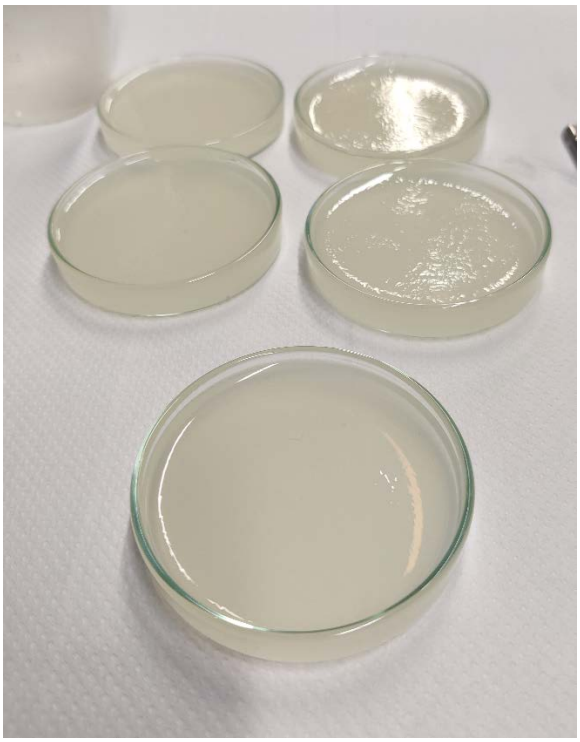


Fig. 2.4. Agarose gels that were set in the petri dish

All the subsequent agarose gels made for the rest of the experiments followed the exact technique detailed above, including the use of the silicone moulds and the gels would roughly take between 40 min to 1h to fully set before their utilization.

2.4.3. Loaded Agarose Gels…

3 more batches of agarose gels were prepared in the same manner excepting that this time each batch was ‘loaded’ with an active cleaning agent (mainly alcohols; butanol, isopropanol, and also acetone). This was achieved first by separately mixing 10% (volume) of each alcohol in the appropriate amount of distilled water. Then each of the alcohol solution was mixed into the double boiled agarose solution (separately) before letting them gel.

In this manner, a 3% agarose gel loaded with butanol gel was obtained, and so also a 3% agarose gel loaded with isopropanol (IPA). However, the 3% agarose butanol and IPA gels proved to be a bit more fragile than necessary, and it was mentioned by Cremonesi that a higher concentration of agarose produces a stiffer/brittle gel among other things, so for the acetone gel, the concentration of the agarose was reduced to 2% (Cremonesi, 2017).

2.5. Polyacrylamide Gels…

2.5.1. General Method of Preparation…

The method of preparation of polyacrylamide gels was completely different to that of the agarose gels and in general was a much more complex procedure owing to the very specific quantities/ratios needed of the materials involved. i.e., acrylamide, bis-acrylamide, ammonium peroxodisulphate (APS), and tetramethyl ethylenediamine (TEMED).

Ratios; acrylamide / bis-acrylamide – 30:0.8, APS – 1.5%, TEMED – 10µl.

The procedure of gelling involves only the proper measuring of the above mentioned ‘ingredients’ after which the necessary amount of distilled water is added, and perhaps even a cleaning solution to load the gel, before thoroughly mixing the solution and letting it gel in the required form. Once again, the ratio between the quantity of acrylamide to water determines the gel percentage (ex:- 10g of acrylamide in 100mL of water yields a 10% gel). And increasing or decreasing the ratio of APS and TEMED (both of which are the polymerizing agents) proportionally increases or decreases the gelling ability of the solution (Baglioni, 2012).

2.5.2. Unloaded/Plain Polyacrylamide gel…

A 5% unloaded/plain polyacrylamide gel was made using 1g of acrylamide to 0.027g of bis-acrylamide along with 0.5g of APS (2% instead of 1.5%), all combined thoroughly in 20mL of distilled H_2O before the addition of 15µl of TEMED (instead of 10µl). On the first attempt of making the polyacrylamide gel, the solution did not gel even after 4 hours of setting time and hence the percentages of APS and TEMED were increased in order to shorten the gelling time, since both APS and TEMED are the active polymerizing agents. This solution (with a higher concentration of APS and TEMED) worked much better as it had already semi-gelled whilst being poured into the silicone moulds (also not ideal). In total the gel was completely ready to use in under 5 min. Since the margin of error (for the solution to gel as it was still being mixed and before it could be poured measuredly into the moulds) was too low, the concentrations of APS and TEMED were once again readjusted (lowered) to suit for a slower gelling time for all further prepared polyacrylamide gels.

2.5.3. Loaded Polyacrylamide gels…

Once again 3 more batches of 5% polyacrylamide gels were prepared in the same manner using the same ratios but with the inclusion of butanol, isopropanol and acetone (10% sol.) separately.

All of the loaded gels poured into the silicone moulds (total 6 gels, see fig. 2.5) took roughly 2 ½ hours to completely gel before they were usable. Note, that most if not all of the chemical compounds used in the preparation of polyacrylamide gels are deemed extremely toxic and hazardous to health, therefore, utmost care was

taken in the handling of said compounds including the use of laboratory grade latex gloves at all times.

Fig. 2.5. All 6 polyacrylamide gels poured into the silicone moulds; 2 butanol gels (Left), 2 IPA gels (Centre), 2 acetone gels (Right).

2.6. Applicational Mode of Gels on Mock-ups…

2.6.1. Applying Agarose Gels…

In total 4 batches of agarose gels were made; plain/unloaded agarose gels, and agarose gels loaded with 10% butanol, isopropanol and acetone respectively.

The unloaded agarose gels were applied on two samples (labelled '1/2' & '1') by gently laying the gels flush on the surface of the canvas (no mechanical intervention was used and the same is true for all samples treated in this thesis). Sample '1/2' was only partially covered (only one half of the circular canvas area) as this was thought to make the difference between the treated and untreated area clearer and more apparent. Sample '1' was completely covered in the agarose gel

and both samples were set aside for a period of 2h undisturbed. After such time the agarose gels were gently lifted from the sample surface and the samples themselves were stored away in Ziplock bags for later analysis.

Each of the loaded agarose gels (butanol, IPA & acetone) were tested on the mock-ups for three different time durations i.e., 5min, 1h, and 3 days using the same application technique mentioned above.

The treated samples are as follows:

A 3% agarose butanol gel was used to treat sample ‘C’ for 5min, sample ‘D’ for 1h and sample ‘E’ for 3 days. Samples ‘C’ and ‘D’ were only half covered (see fig. 2.6) with the gel whereas sample ‘E’ was fully covered (and stored in a Ziplock bag for the duration of the treatment). Again, no mechanical intervention was used and the samples were stored away in Ziplock bags once the gels were removed.

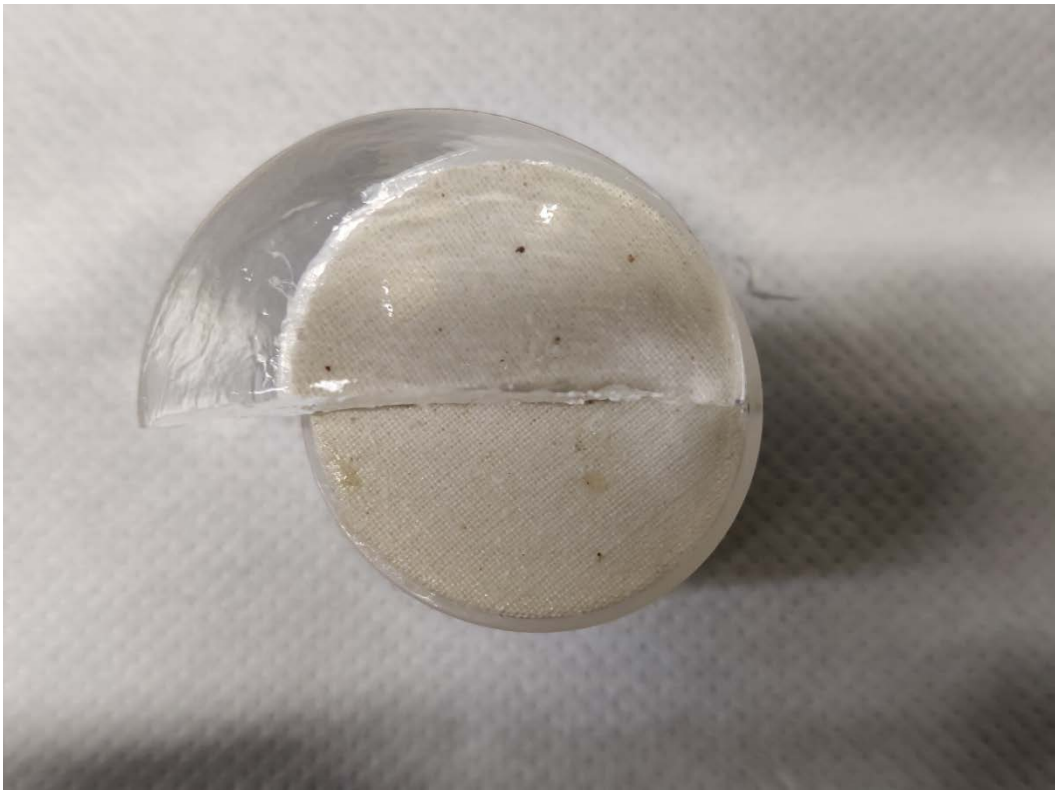


Fig. 2.6. Top view, example of a mock-up canvas sample only half covered by a gel.

A 3% agarose isopropanol gel was used to treat sample ‘F’ for 5min, sample ‘G’ for 1h and sample ‘H’ for 3 days. Samples ‘F’ & ‘G’ were only half covered whereas sample ‘H’ was fully covered. A different technique of agarose gel application was used on the fully covered sample ‘H’, where, instead of placing a fully formed piece of gel on the canvas surface, a gel solution that was still semi-solid was “poured” onto the mock-up canvas (see fig. 2.7). This technique of applying semi-gelled agarose by pouring it onto a surface was recommended for better and more even contact between the gel and the applied surface (Cremonesi, 2017). And indeed, the poured agarose gel (on sample ‘H’) did show clear sings of better contact between gel and surface (see fig. 2.8).

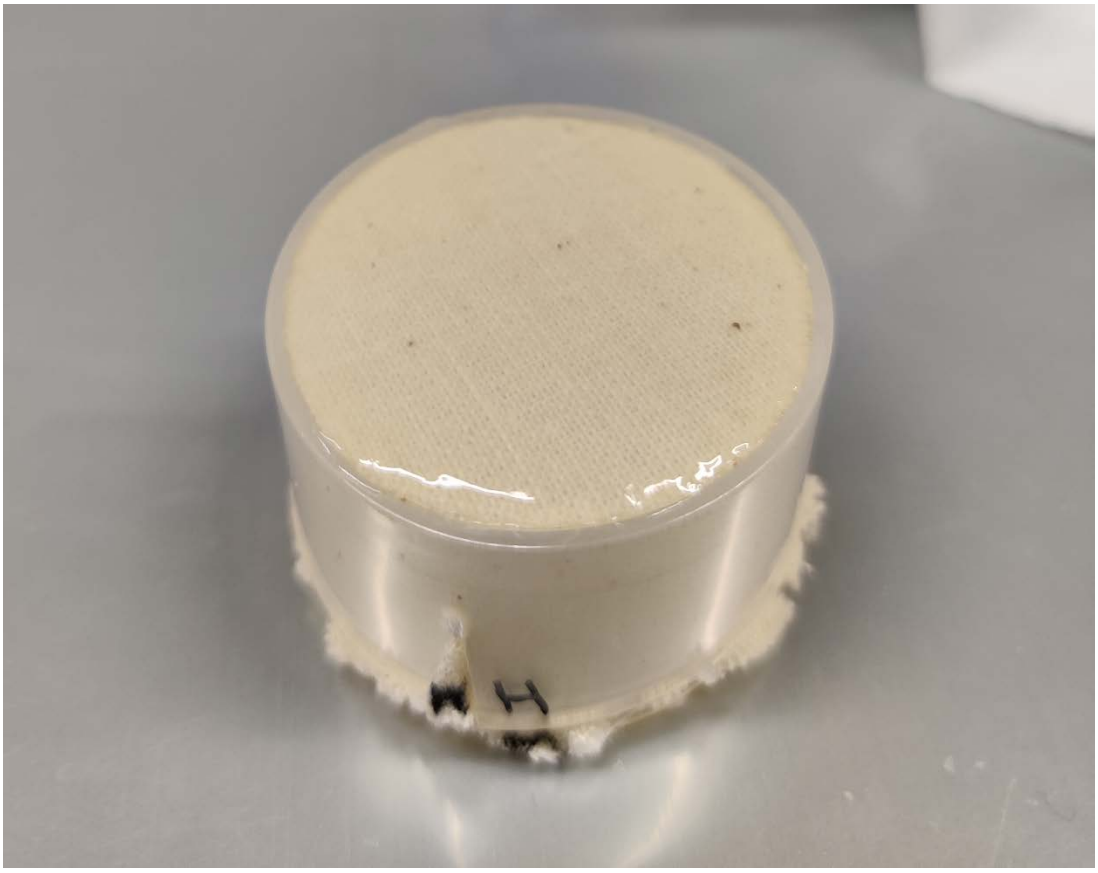


Fig. 2.7. Sample ‘H’ with the agarose gel poured on top (gel is noted by the light reflected toward the bottom of the canvas surface).

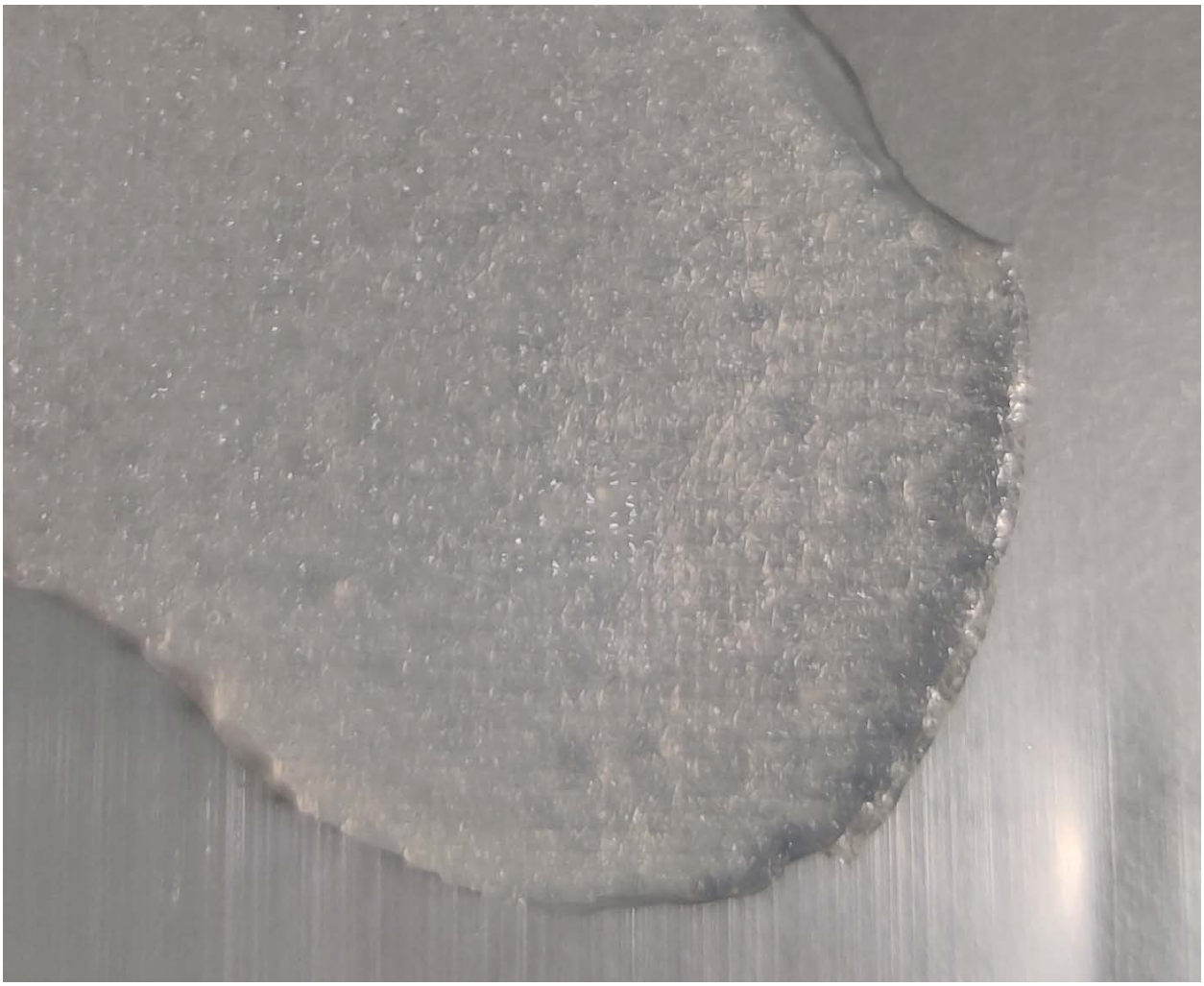


Fig. 2.8. Contact side of gel after removal from sample ‘H’, note the texture of the gel which is a near perfect imprint (negative) of the cotton canvas surface texture.

A 2% agarose acetone gel was used to treat sample ‘I’ for 5 min, sample ‘J’ for 1h and sample ‘K’ for 3 days. All samples were only half covered and treated using the earlier method of placing fully formed gels onto the canvas surface.

A summary of the treated samples is given below;

Table 2.1. List and details of all loaded agarose gel treated samples.

Type of gel	Duration of application		
	5min	1 hour	3 days
3% agarose butanol gel	‘C’	‘D’	‘E’
3% agarose isopropanol gel	‘F’	‘G’	‘H’
2% agarose acetone gel	‘I’	‘J’	‘K’

In this manner samples ‘C’ through ‘K’ were treated and stored away in Ziplock bags for further analysis and the agarose gels used for said treatment were also stored away in Ziplock bags in a refrigerator concluding the testing of the agarose gels.

2.6.2. Applying Polyacrylamide Gels…

The method of application of polyacrylamide gels (loaded and unloaded) onto the mock-ups was the exact same technique used for the agarose gels mentioned prior. The gels were merely placed on the canvases (not poured) without any

mechanical intervention and all the samples were only half covered (see fig 2.9), again for clarity purposes.

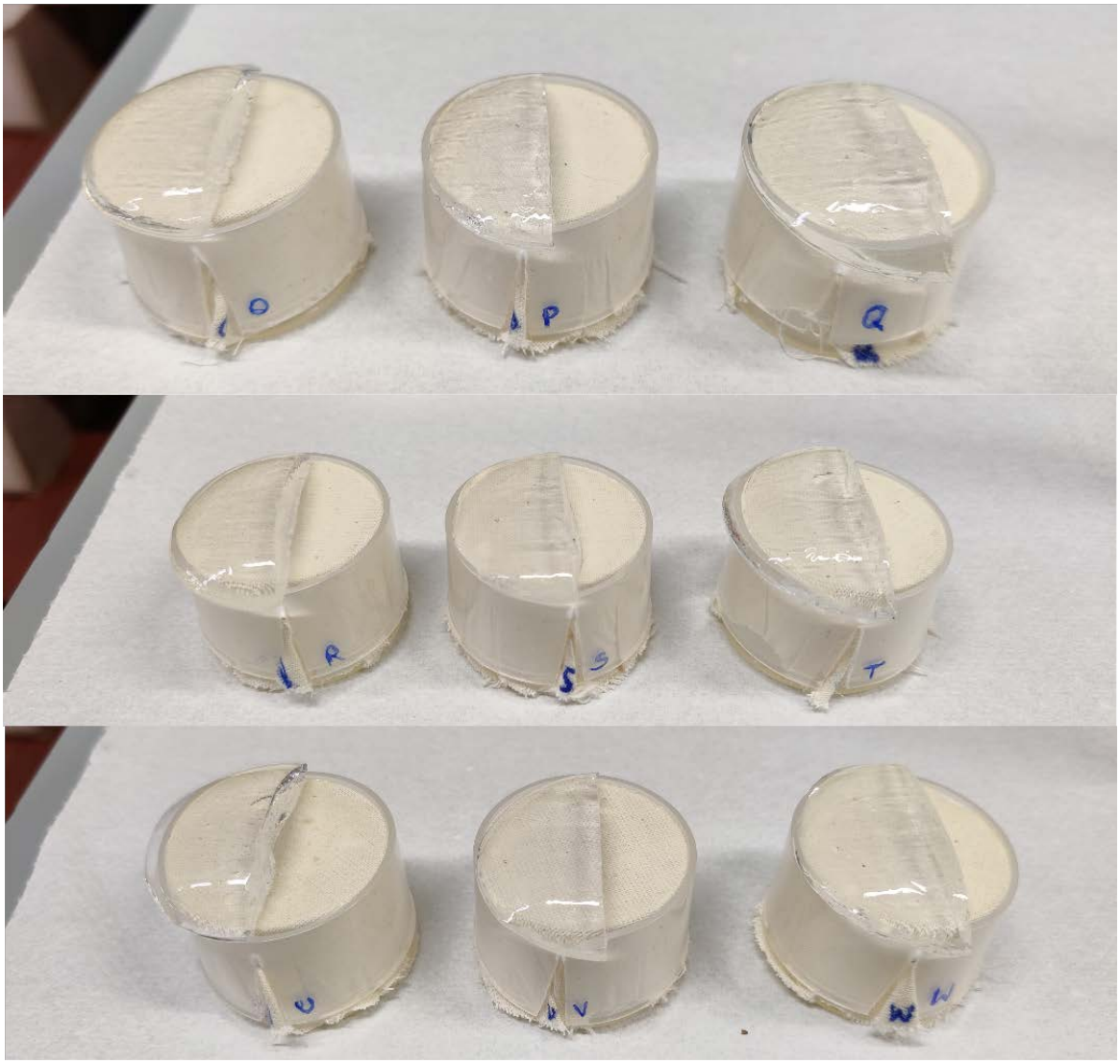


Fig. 2.9. All loaded polyacrylamide treated samples (‘O’ through ‘W’, from top left to bottom right), note they are only half covered.

A summary of the treated samples is given below;

Table 2.2. List and details of all polyacrylamide gel treated samples.

Type of gel	Duration of application		
	5min	1 hour	3 days
Unloaded/plain 5% polyacrylamide gel samples labelled	'M'	'N'	---
5% polyacrylamide butanol gel	'O'	'P'	'Q'
5% polyacrylamide Isopropanol gel	'R'	'S'	'T'
5% polyacrylamide acetone gel	'U'	'V'	'W'

All tested samples ('O' through 'W') were stored away in Ziplock bags and the used polyacrylamide gels were placed in the refrigerator. The handling of any and all samples and the gels (both of agarose and polyacrylamide) were done always with latex gloves in order to not contaminate the gels nor the samples themselves and also for safety concerns. This concludes the testing of the polyacrylamide gels.

CHAPTER 3
RESULTS AND DISCUSSION

The results presented in this chapter are aimed towards the main objective of the present thesis, which was to formulate cleaning solutions in order to test their efficiency in the removal/stabilization of certain salts (specifically calcium and magnesium sulfates). For this purpose, mock-up samples with salts were created. and, the method in which the cleaning solutions were to be applied on the mock-ups was determined to be through the media of agarose and polyacrylamide gels. These gels act as *sponges* which can be loaded with the formulated solutions to test their efficiency individually and in a very controlled and repeatable manner.

The results were obtained through the following analytical techniques; FT-IR-ATR, X-Ray Diffraction, SEM-EDS and also the HIROX digital microscope for when high magnification and resolution colour images were required.

The analysis of the various gel treated mock-ups by SEM-EDS and XRD are made at several time steps, and therefore, some of these data are reported in the appendix. While, all data that was pertinent to the performance of the various agarose and polyacrylamide gels and their impact (positive or negative) on the sample mock-ups have been detailed below.

Keeping in mind the main objective of the present thesis, two things were critical in order to fulfill this objective. First was the creation of the imitation sample mock-ups and second was the experimental treatments conducted on these mock-ups using the various formulations of the loaded and unloaded agarose and polyacrylamide gels. With this in mind the results are presented as follows.

3.1. Characterization of mock-ups by FT-IR-ATR, XRD & SEM-EDS…

FT-IR-ATR, XRD, and SEM-EDS were used for the characterization of the pure cotton canvas, dolomitic lime, casein, the mock-up canvas after the application of a layer of dolomitic lime and casein (i.e., prepared cotton canvas), and lastly the sample mock-up itself (i.e., the prepared cotton canvas after the formation of salts).

3.1.1. Cotton Canvas Characterization…

FT-IR-ATR…

The core of cotton is mainly composed of cellulose and outside there resides in small amounts noncellulosic materials such as waxes, pectin and proteins (Nevell & Zeronian, 1985).

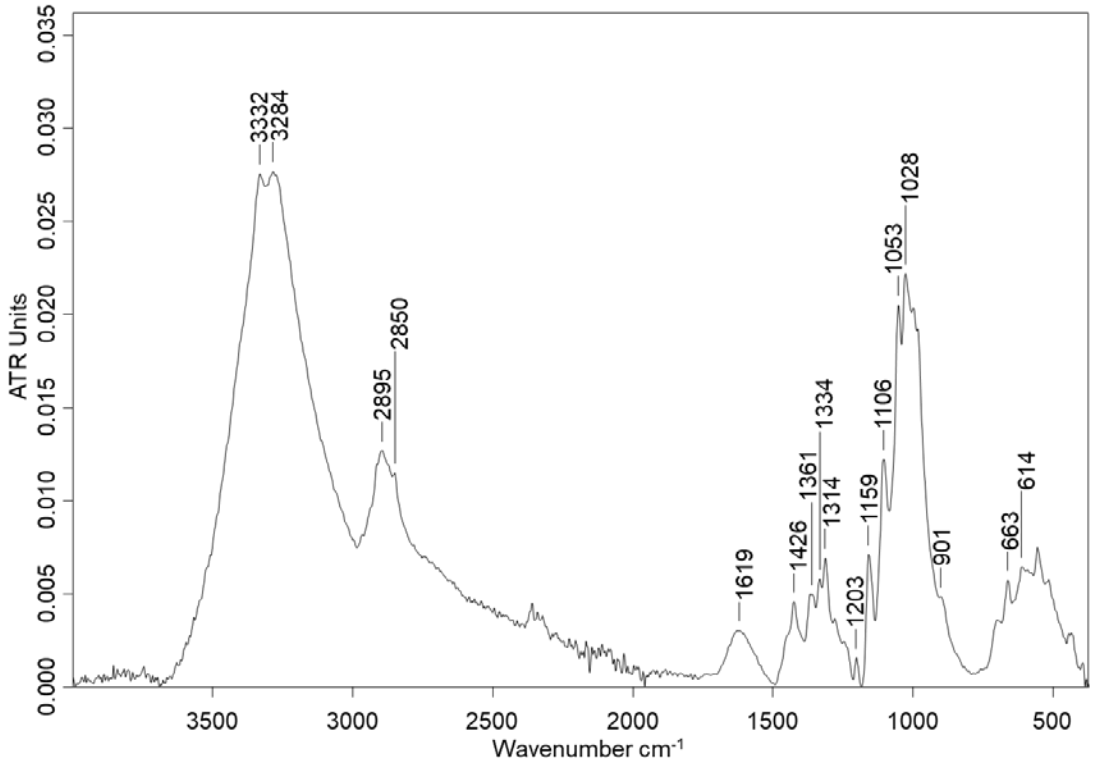


Fig. 3.1. FT-IR-ATR spectra of cotton canvas / cellulose.

Table 3.1. Infrared absorption frequencies of cellulose and other impurities (Chung, 2004).

ATR (cm^{-1})	Literature (cm^{-1})	Peak characteristics
3332–3284	3570–3200	H-bonded OH stretch
2895–2850	3000–2800	C–H stretching
	1650–1633	Adsorbed H_2O
1619		Asym. carboxylate stretch
1426	1430	CH wagging (in-plane bending)
1361	1372	CH bending (deformation stretch)
1334	1336	OH in-plane bending
1314	1320	CH wagging
	1282	CH deformation stretch
	1236	OH in-plane bending
1203	1204	OH in-plane bending
1159	1178	Asym. Bridge C–O–C
1106	1130	Asym. Bridge C–O–C
1053	1092	Asym. In-plane ring stretch
1028	1042	C–O stretch
	998–1002	C–O stretch
901	898	Asym. out-of-phase ring stretch: C_1–O–C_4; b glu-cosidic bond

XRD…

The XRD analysis of the cotton canvas showed peaks typical of pure cotton, where two relatively low intensity peaks appear between 14-17 2theta value, and a much larger peak at around 22 2theta value (Yazdanshenas, 2013). These peaks of cotton will also appear in all subsequent XRD diffractograms of the analyzed sample mock-ups.

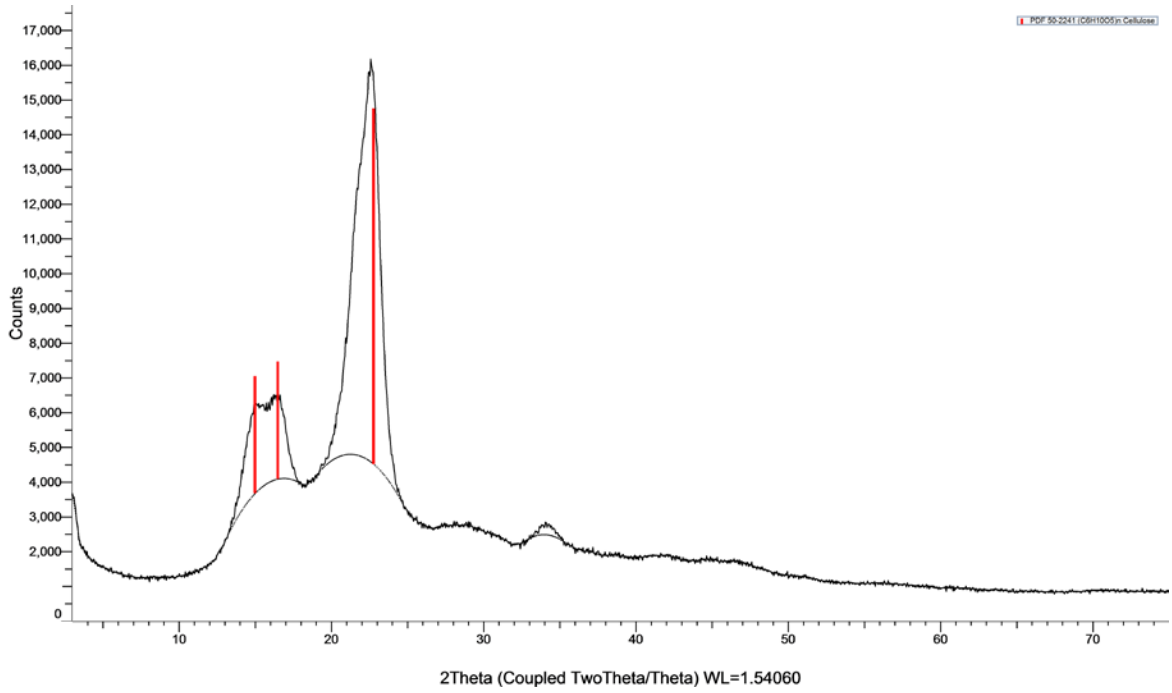


Fig. 3.2. Diffractogram of pure cotton, showing peaks of cellulose.

SEM-EDS…

An area of pure cotton canvas was scanned (see fig. 3.3 & 3.4) and also the cross section of cotton fibers was observed under high magnification, showing typical morphology of cotton fibers (see fig. 3.5).

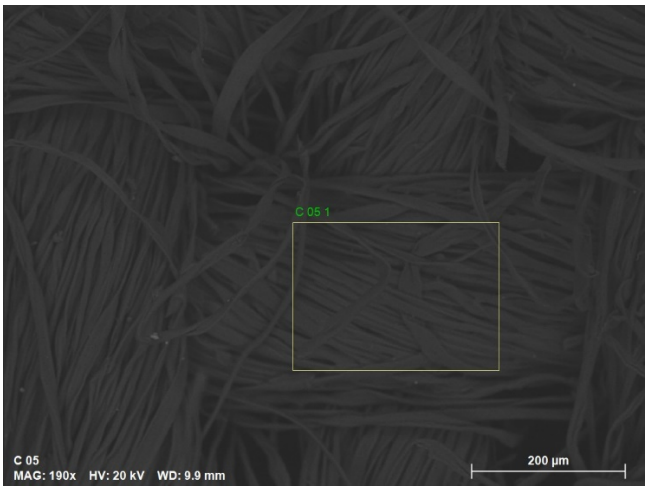


Fig. 3.3. SEM image of surface of pure cotton, yellow box indicating the scan area.

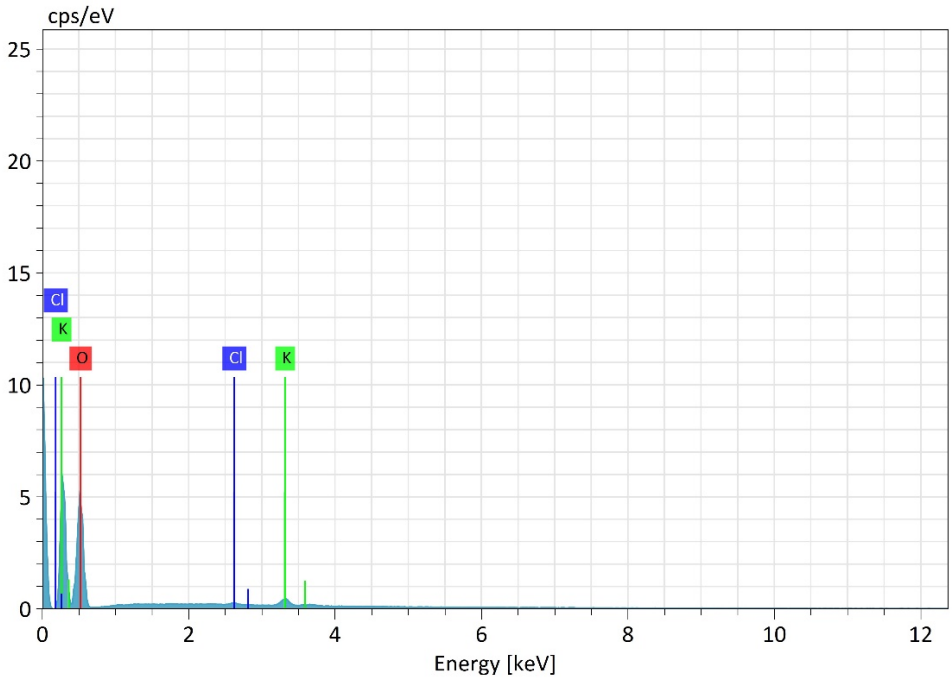


Fig. 3.4. SEM-EDS spectra of scanned area of pure cotton.

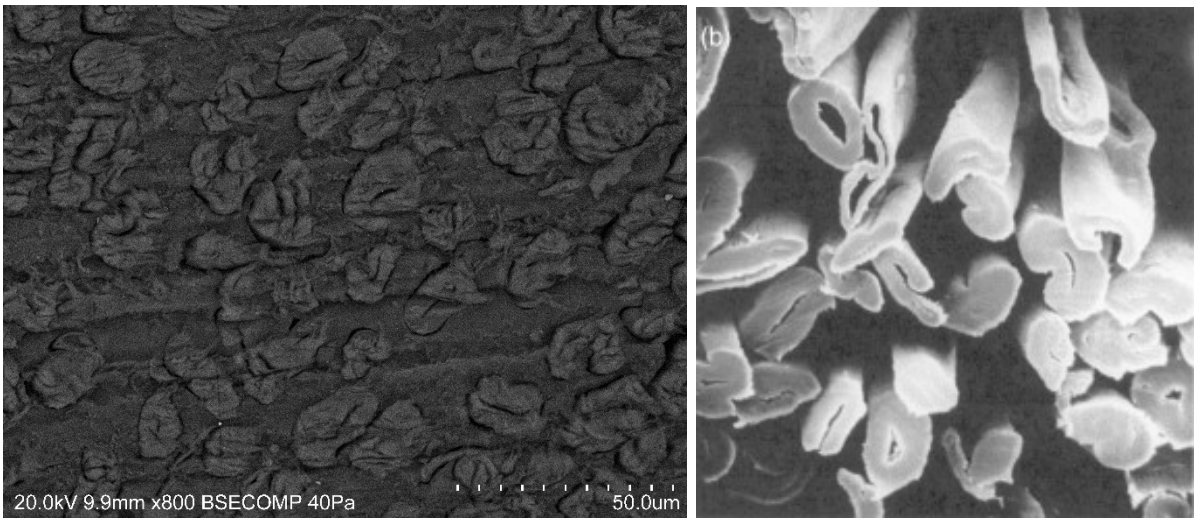


Fig. 3.5. SEM image, cross-section of cotton fibre that are kidney-shaped. left image from analysis, right from (Candido, 2021).

3.1.2. Dolomitic Lime Characterization…

FT-IR-ATR…

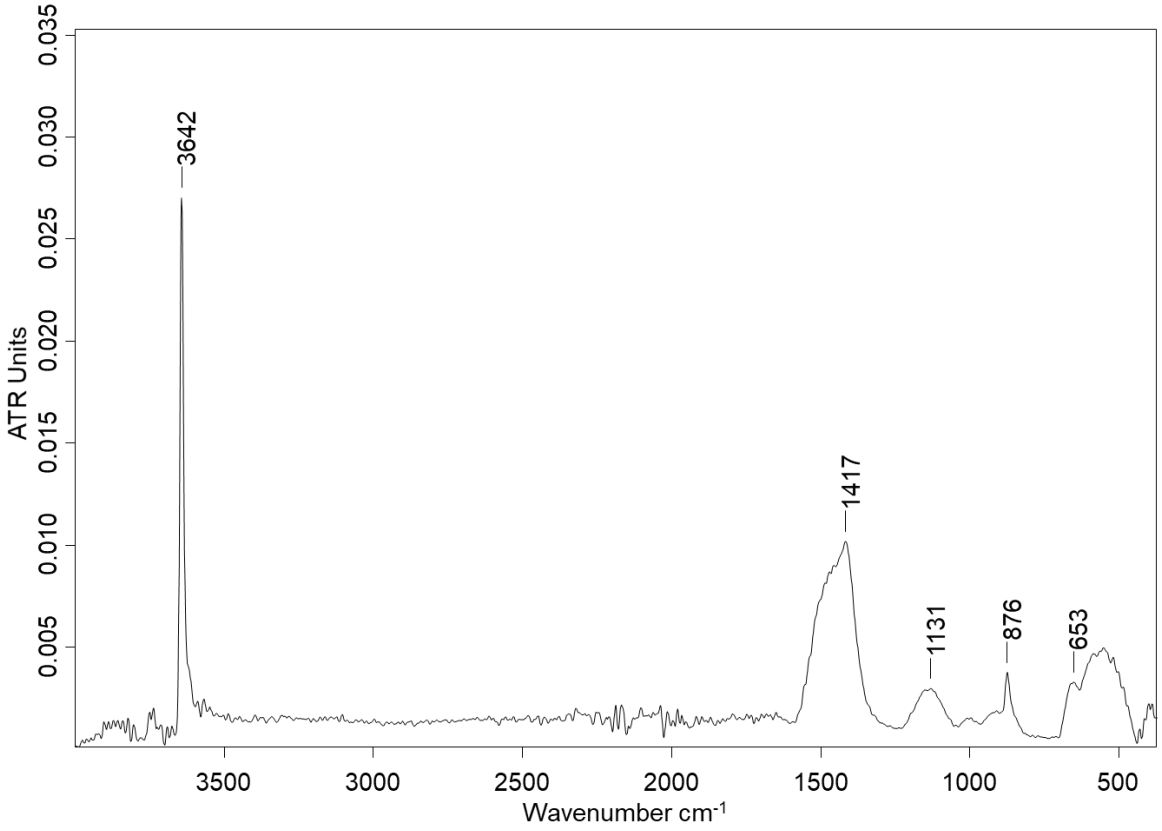


Fig. 3.6. FT-IR-ATR spectra of Dolomitic lime / Portlandite.

In Fig. 3.6. the narrow O-H band at 3642cm^{-1} indicates the presence of portlandite, the broad signal at 1417cm^{-1} can be attributed to C-O band of calcite and monocarboaluminates, and the broad bands between 800-1300cm^{-1} with a *shoulder* at 1131cm^{-1} can be assigned to S-O antisymmetric stretching vibrations of SO_4^{2-} and another shoulder at 876cm^{-1} can be assigned to C-O stretch of (CO_3^{2-}) (Zarzuela, 2020).

XRD…

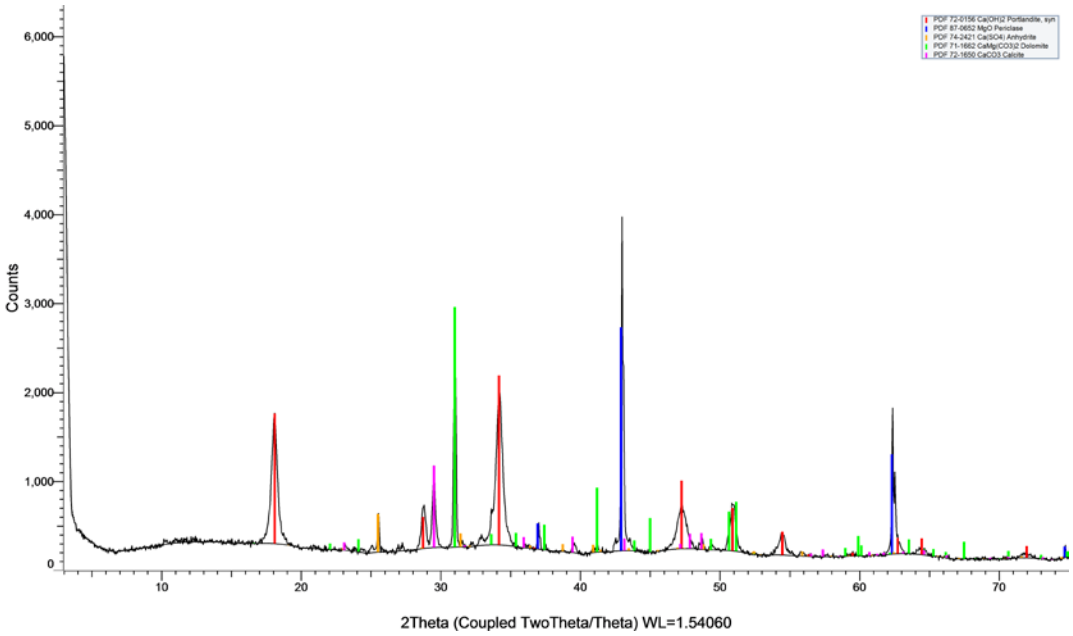


Fig. 3.7. Diffractogram of Dolomitic Lime, showing peaks of Portlandite ($Ca(OH)_2$), Periclase (MgO), Anhydrite ($Ca(SO_4)$), Dolomite ($CaMg(CO_3)_2$), and Calcite ($CaCO_3$).

The above figure details the mineralogical composition of the dolomitic lime used in the process of creation of the mock-ups. Showing the presence of mainly portlandite, periclase, dolomite and also calcite, along with the hydrate phase of calcite (Bamogo, 2022).

3.1.3. Casein Characterization…

FT-IR-ATR…

Casein is a fine white to yellowish powder (a protein) derived from water-soluble lactic acid often used as a binder in combination with other materials. It contains sulfur and phosphorus. Casein itself is insoluble in water and alcohol but is soluble in carbonates and other alkali solutions. It has strong adhesion since it becomes insoluble in water again after drying (Derrick, 1999).

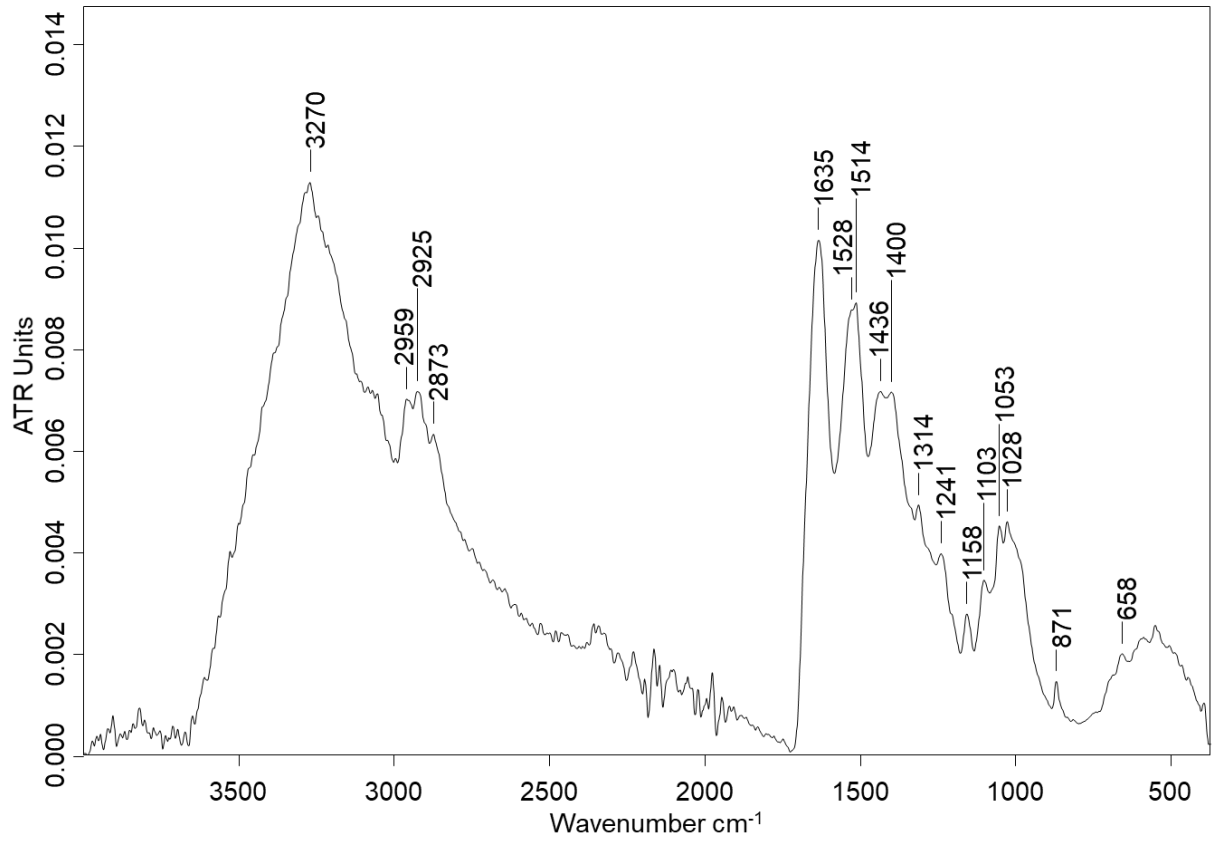


Fig. 3.8. FT-IR-ATR spectra of casein.

Table 3.2. Infrared absorption frequencies of casein (Derrick, 1999).

ATR (cm^{-1})	Literature (cm^{-1})	Peak characteristics
3270	3400–3200	N-H stretching bands
2959-2873	3100–2800	C–H stretching bands
1635	1660-1600	C=O stretching bands
1514	1565-1500	C-N-H bending band
1436-1314	1480-1300	C-H bending band

In fig. 3.8. proteins are characterized by the presence of amide I peak at 1635cm^{-1} and an amide II peak at 1528cm^{-1}. Only FT-IR-ATR was used to characterize the casein.

3.1.4. Prepared Cotton Canvas Characterization…

FT-IR-ATR…

The prepared canvas is the sample mock-ups just prior to the introduction of pure SO_2 gas for salt formation, in other words it is the cotton canvas primed with a dolomitic and casein layer.

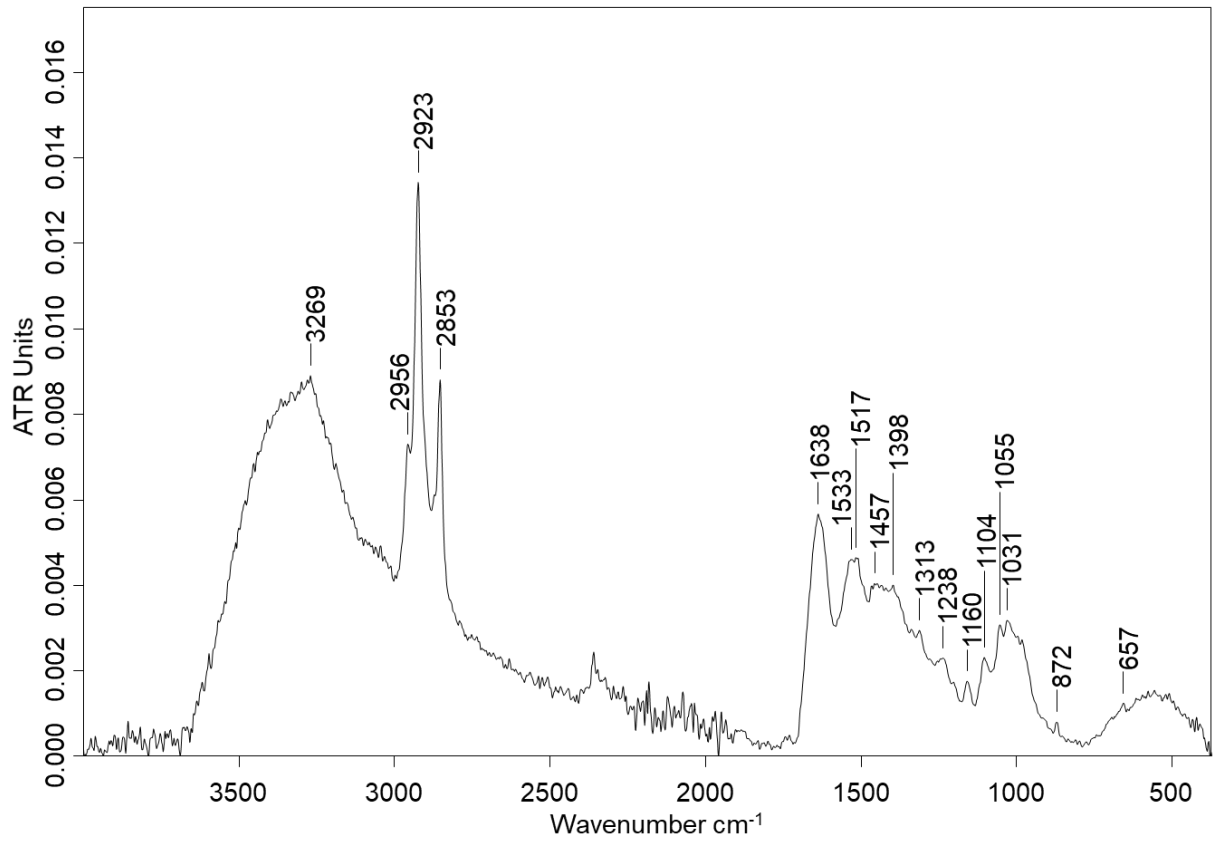


Fig. 3.9. FT-IR-ATR spectra of the prepared cotton canvas.

In Fig. 3.9. the infrared absorption bands for the prepared cotton canvas mainly coincides with the same bands and peaks as the previously analyzed casein and cotton canvas (cellulose). In other words, the same protein peaks of amide I can

be observed at 1638cm^{-1} and an amide II peak at 1533cm^{-1}. And peaks that correspond to cellulose can be observed at 1160cm^{-1} of Asym. Bridge C–O–C, 1104cm^{-1} of Asym. Bridge C–O–C, 1055cm^{-1} of Asym. In-plane ring stretch, and at 1031cm^{-1} of C-O stretch.

XRD…

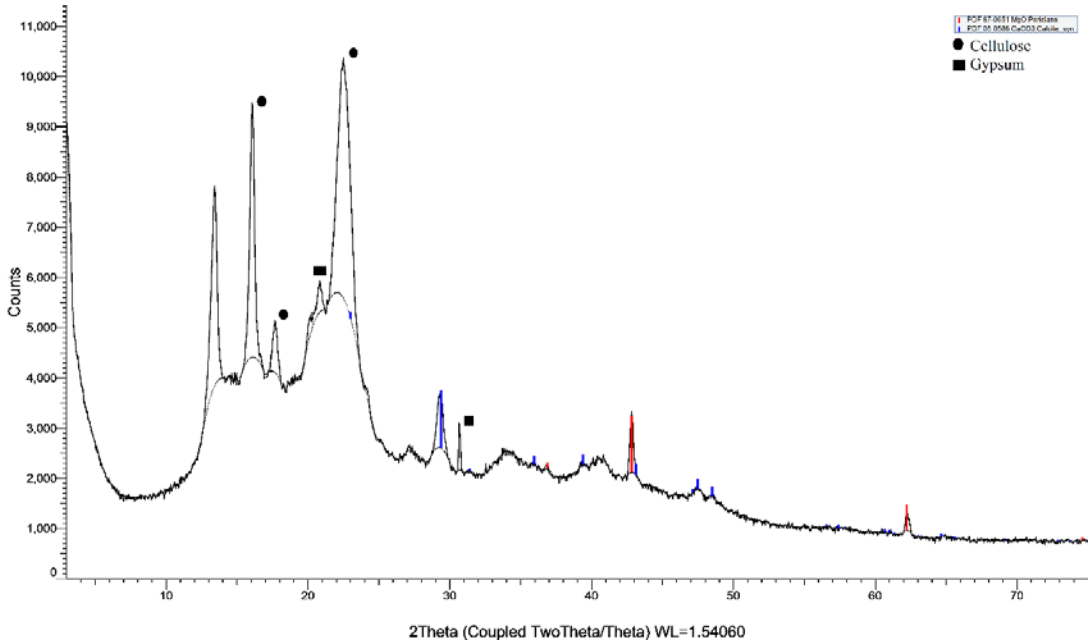


Fig. 3.10. Diffractogram of cotton canvas primed with dolomitic lime and casein, showing peaks of Cellulose, Periclase (MgO), Calcite ($CaCO_3$), and Gypsum ($Ca(SO_4)(H_2O)_2$).

The figure above shows the typical cellulose peaks observed previously in fig. 3.2. Peaks of periclase, calcite and also gypsum a dihydrate phase of calcium sulfate are present from the application of the dolomitic lime layer on the cotton canvas.

SEM-EDS…

The prepared cotton canvas under SEM imaging showed mostly a flat and homogenous surface layer (made of dolomitic and casein) along with a few cracks and superimposed cotton fibres (see fig. 3.11).

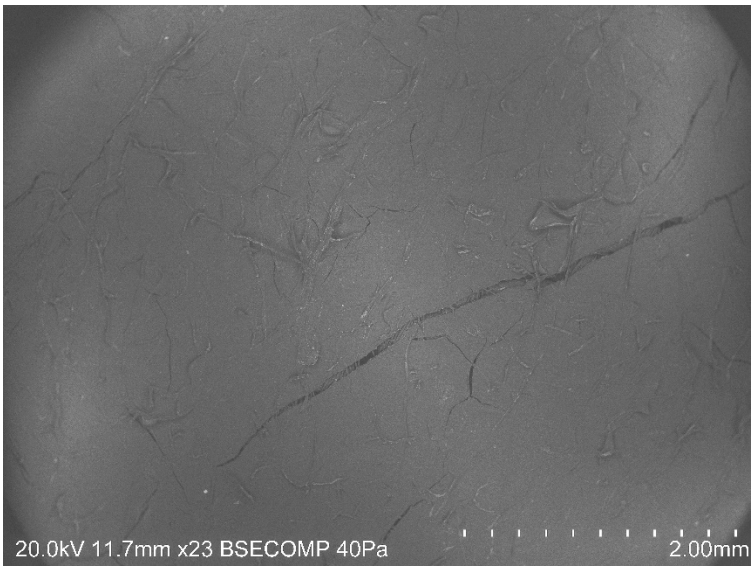


Fig. 3.11. SEM image, surface of sample mock-up before formation of salts.

An area scan of the surface showed that there were in very small amounts magnesium, phosphorus, sulphur and calcium. (see fig. 3.12).

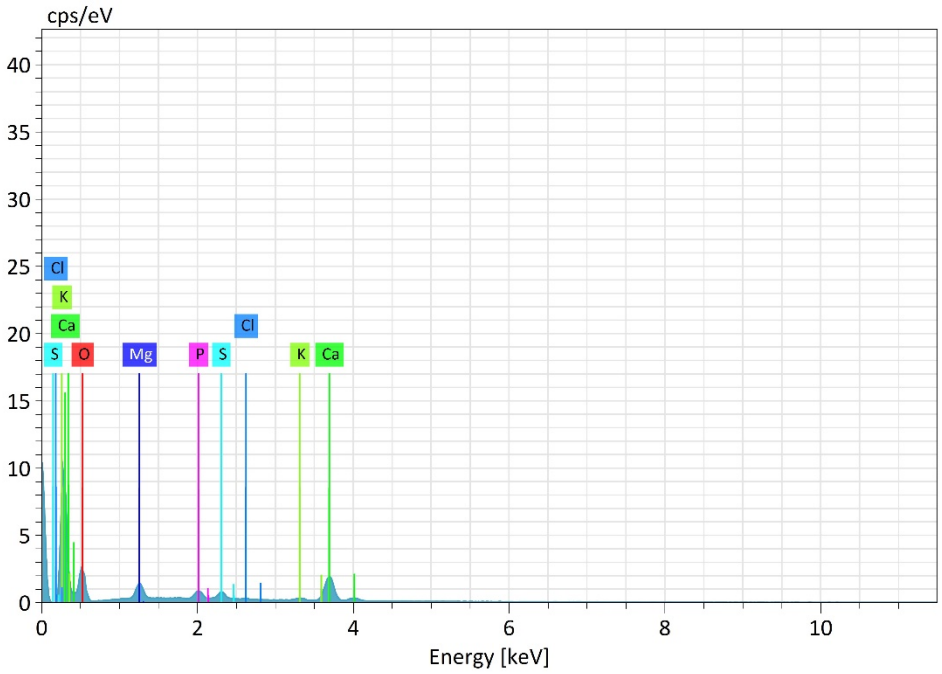


Fig. 3.12. SEM-EDS, area scan of dolomitic casein layer showing among other elements some Mg, P, S, and Ca.

3.1.5. Sample Mock-up Characterization…

XRD and SEM-EDS was used to characterize the sample mock-ups after the formation of salts.

XRD…

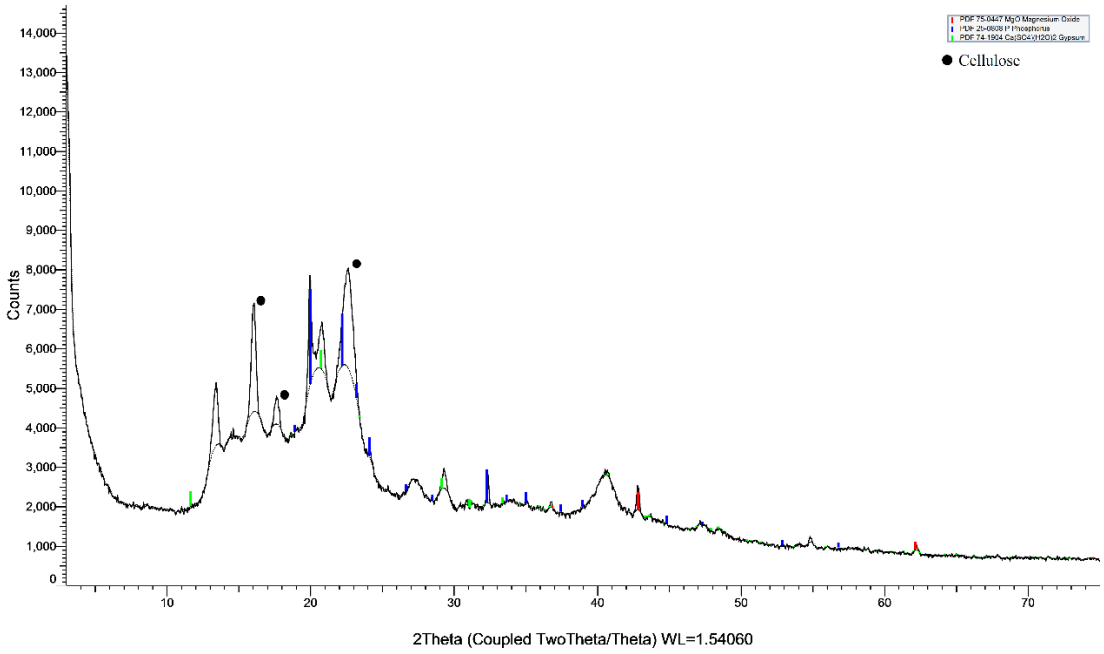


Fig. 3.13. Diffractogram of final version of the mock-up after salt formation, showing peaks of Cellulose, Magnesium Oxide (MgO), and Gypsum ($Ca(SO_4)(H_2O)_2$).

In the above figure note the peaks of gypsum at 2theta values of 21 and 29 roughly, which is a dihydrate calcium sulfate.

SEM-EDS…

The final version of the sample mock-ups, meaning, the prepared cotton canvas after the inducing of SO_2, but before any gel treatment was analyzed for the confirmation of salt formation. Both calcium sulfates and magnesium sulfates were noted. Many ring-like formations of small crystalline material were noted and EDS mapping suggested that they were calcium sulfates (see fig. 3.14). while, a more

ambiguous structure that was surrounded by calcium sulfates was observed and scanned to be magnesium sulfates (see fig 3.15 & 3.16).

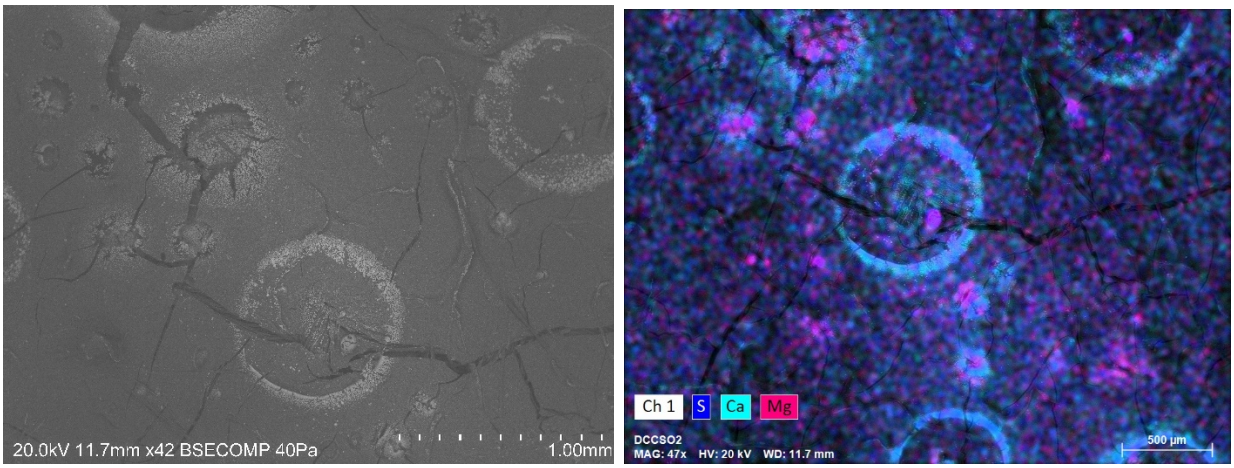


Fig. 3.14. SEM image of ring-like formation of salts (left), EDS mapping of same ring-like formations showing elements S, Ca, and Mg (right).

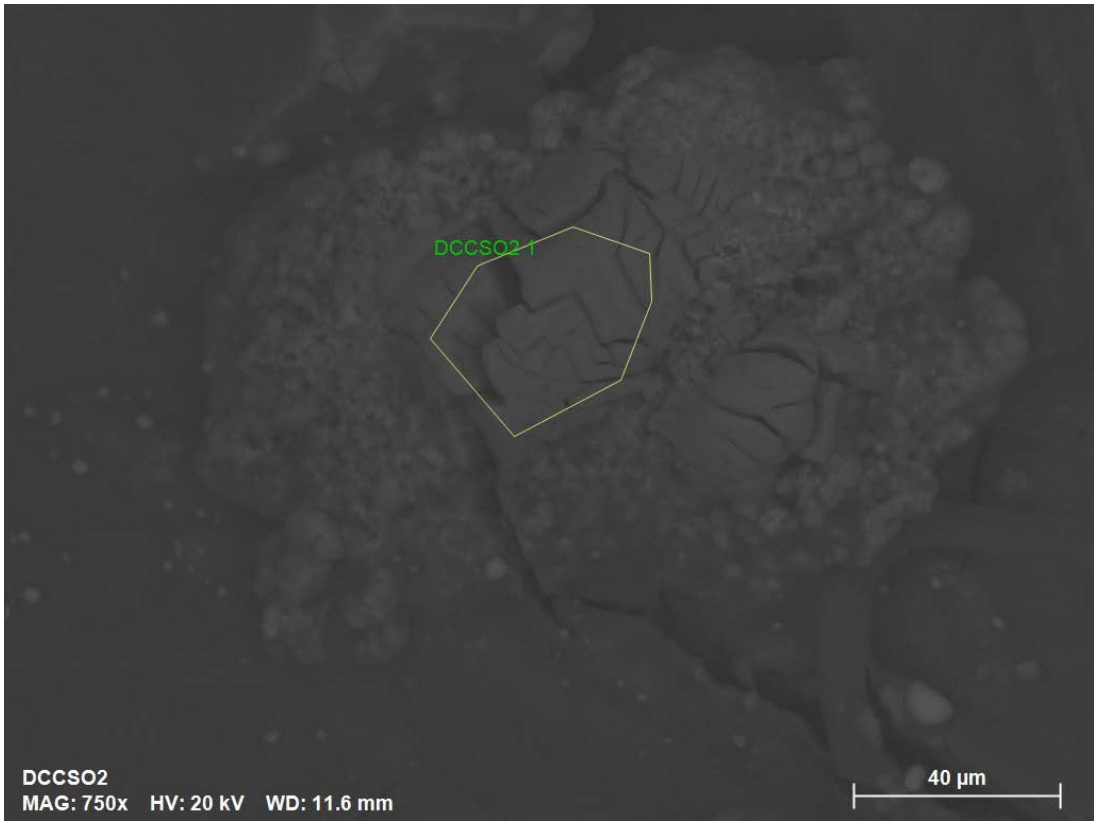


Fig. 3.15. SEM image of magnesium sulfate surrounded by smaller calcium sulfates.

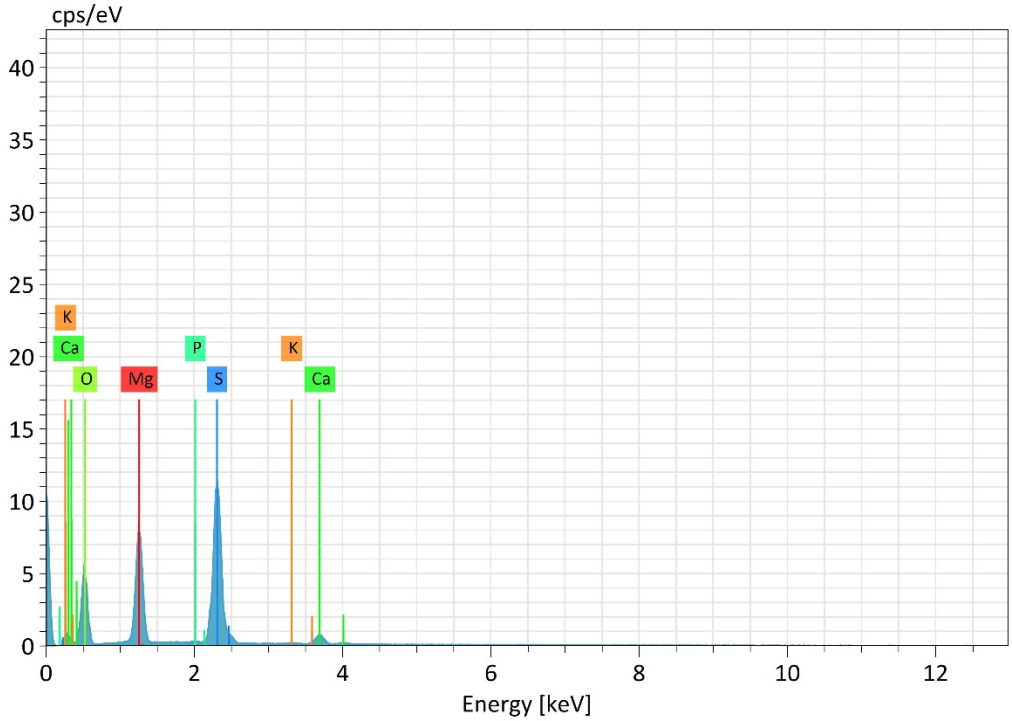


Fig. 3.16. EDS area scan of Magnesium sulfate (of fig. 3.16) showing relatively high amounts of elements Mg and S, as compared to Ca.

The analytical characterization of the imitation mock-ups and its various components are concluded with the final SEM-EDS analysis of the sample mock-ups which confirmed the presence of both calcium and magnesium salts necessary for experimentation.

3.2. Types of Gels Used…

The method of preparation of the various gels used are detailed in methodology section of chapter 2, and hence will not be detailed again. But, an overview of the various types and combinations of gel and cleaning solution is provided.

Two types of gels were chosen to act as vehicles to deliver three different cleaning solutions. The gels were made of agarose and polyacrylamide while the cleaning solutions were butanol, isopropanol and acetone (as they are all commonly used cleaning alcohols).

To act as a control for the gel treatment experiments, firstly unloaded or plain versions of both gels were created. Meaning, a 4% agarose gel without any cleaning solution and a 5% polyacrylamide gel, also without any cleaning solution.

To create agarose and polyacrylamide gels loaded with a cleaning solution, firstly 10% solutions (to obtain a mild cleaning agent) of butanol, isopropanol and acetone were made. And then, each of the alcohol solutions were loaded into the agarose and polyacrylamide gels (process detailed in chapter 2) creating six unique gels for experimental purposes;

In total considering the unloaded and loaded gels of both agarose and polyacrylamide, 8 unique gels were created for their testing on the mock-ups:

Table 3.3. List of all agarose and polyacrylamide gel formulations.

Unloaded / plain 4% agarose gel	Unloaded/plain 5% polyacrylamide gel
3% agarose butanol gel	5% polyacrylamide butanol gel
3% agarose isopropanol gel	5% polyacrylamide isopropanol gel
2% agarose acetone gel	5% polyacrylamide acetone gel

The following mock-up samples were tested by the eight unique gels in the following manner;

For the unloaded 4% agarose gels, samples labelled ‘1/2’ and ‘1’ were both treated for 2 hours.

The unloaded 5% polyacrylamide gels were applied on samples ‘M’ and ‘N’ for 5min, and 1h respectively.

Table. 3.4. List and details of all loaded agarose and polyacrylamide gel treated samples.

Type of gel	Duration of application		
	5min	1 hour	3 days
3% agarose butanol gel	‘C’	‘D’	‘E’
3% agarose isopropanol gel	‘F’	‘G’	‘H’
2% agarose acetone gel	‘I’	‘J’	‘K’
5% polyacrylamide butanol gel	‘O’	‘P’	‘Q’
5% polyacrylamide Isopropanol gel	‘R’	‘S’	‘T’
5% polyacrylamide acetone gel	‘U’	‘V’	‘W’

In this manner all of the gels were applied on their respective samples, and once the imitation mock-ups were treated, they were promptly analyzed by SEM-EDS and XRD, the results of which are presented in the following sections.

3.3. Analysis of Agarose Gel Treatments by SEM-EDS & XRD…

3.3.1. Unloaded / Plain 4% Agarose gel…

A 4% unloaded / plain agarose gel was made and tested on two samples (labelled ‘1/2’ & ‘1’) for the time duration of 2h sample ‘1/2’ was only partially covered with the gel while sample ‘1’ was fully covered. The agarose gel treated side of sample ‘1/2’ did show a slight but noticeable reduction in salts, which was evident at the interface of the treated and untreated side (see fig. 3.17).

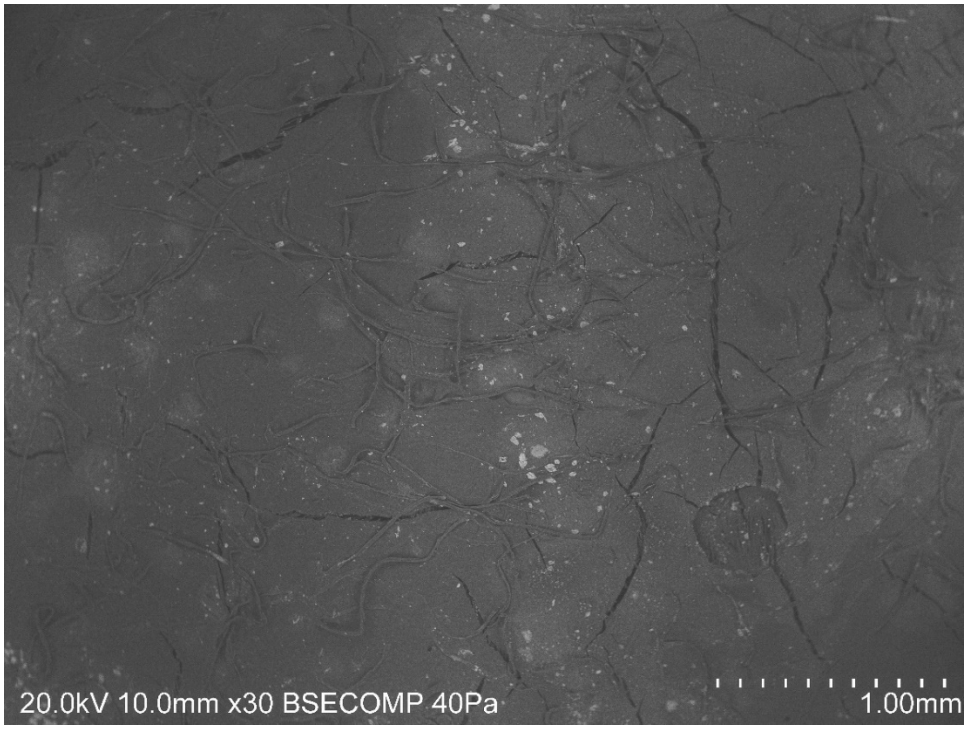


Fig. 3.17. SEM image of sample ‘1/2’ at the interface, showing gel treated side (left) with relatively fewer salts than untreated side (right), with much more salts (note the salts by the light grey patches and the white spots).

However, on further analysis via EDS area scans (see fig. 3.18) of both the agarose gel treated side and the untreated side, it was quite evident that while there was a reduction of salts (and/or elements S, and Ca) on the treated side, it was only a small reduction as compared to many of the other gels tested during the course of this thesis. Also, there is no noticeable reduction of Mg as it is present on treated and untreated sides of all mock-ups usually in equal quantities as it is part of the composition of the dolomitic lime layer applied on the mock-ups.

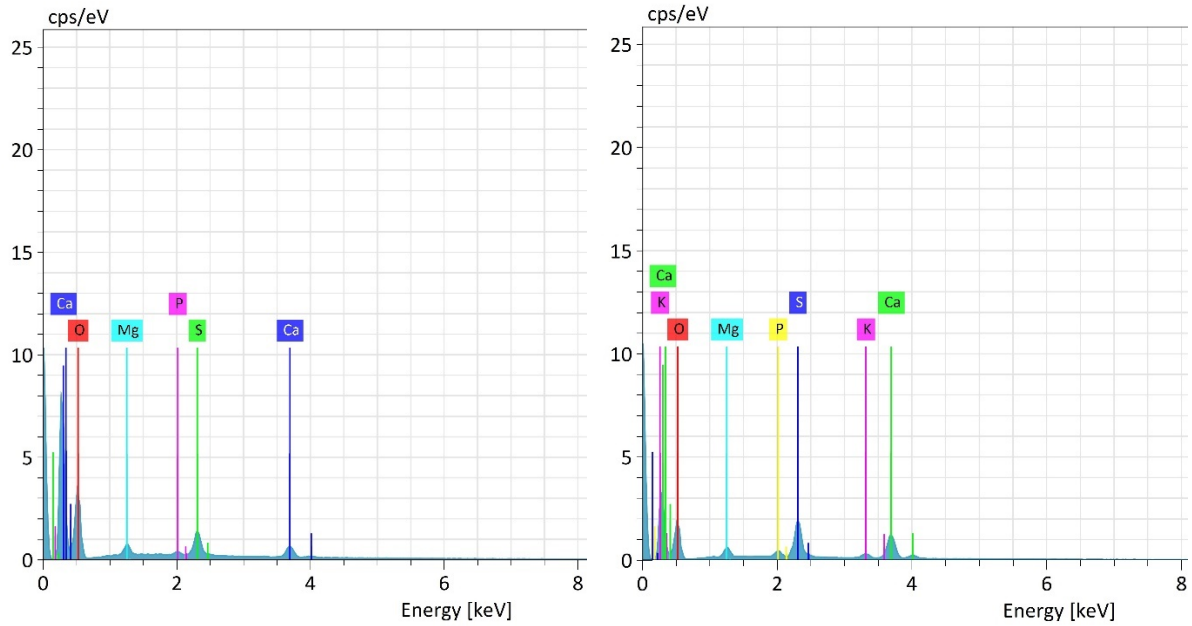


Fig. 3.18. EDS spectra, of sample ‘1/2’, gel treated side (left), untreated side (right), notice the elemental peaks of S, and Ca which are slightly but noticebaly lower on the treated side.

Regarding sample ‘1’ that was also treated with the same 4% plain agarose gel for the same time duration of 2h, but was fully covered by the gel showed no more improvement toward the reduction of salts than sample ‘1/2’. Though the sample mock-up was fully covered by the gel, many areas/scatterings of salts (mostly calcium carbonates and sulfates) were noticed and in general it could be said that both gels on samples ‘1/2’ & ‘1’ performed with similarly poor efficiency in salt removal/reduction.

However, no surface damage was noticed on the treated area of either sample and so the structural integrity of both sample mock-ups ‘1/2’ & ‘1’ remained uncompromised.

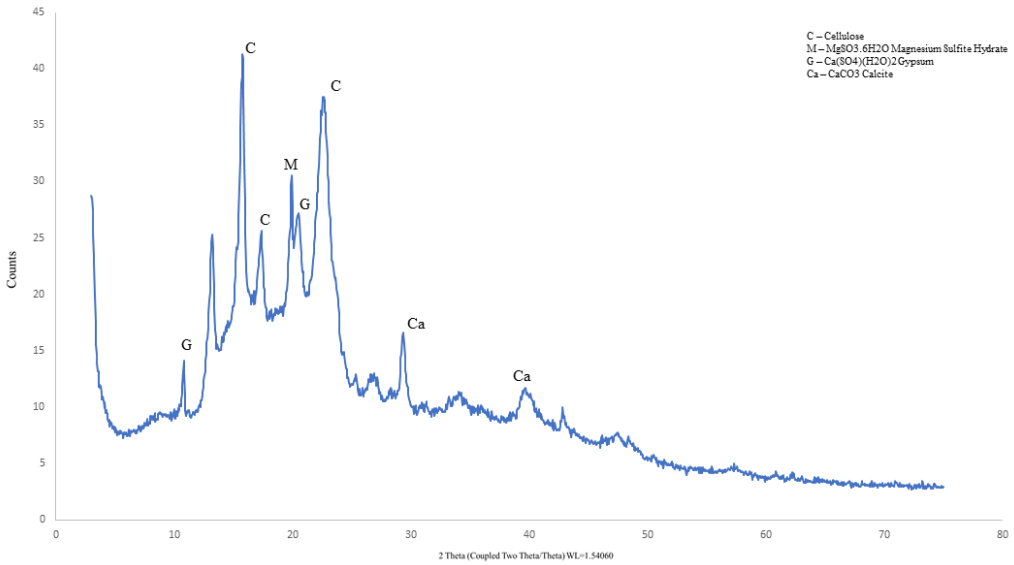


Fig. 3.19. Diffractogram of sample ‘1’, showing peaks of Cellulose, ($MgSO_3.6H_2O$) Magnesium Sulfite Hydrate, ($Ca(SO_4)(H_2O)2$) Gypsum, and ($CaCO_3$) Calcite.

In the figure above, note the presence of calcite at the 2theta value of 30 and also the magnesium sulfite hydrate peak around 2theta value of 20. The peaks are not as weak as it is in other diffractograms obtained from gels that have excellent salt-removal capabilities. Sample ‘1/2’ showed identical cleaning performance as the gel used & time duration of gel application was the exact same as of sample ‘1’.

3.3.2. Loaded Agarose Gels…

3.3.2.1. Gels Applied for 5 minutes…

Three sample mock-ups were treated for the duration of 5min using a loaded agarose gel. Sample ‘C’ was treated with a 3% agarose butanol gel, sample

‘F’ was treated with a 3% agarose isopropanol gel and sample ‘I’ was treated with a 2% agarose acetone gel. Following are their results:

Sample ‘C’ – 3% agarose butanol gel.…

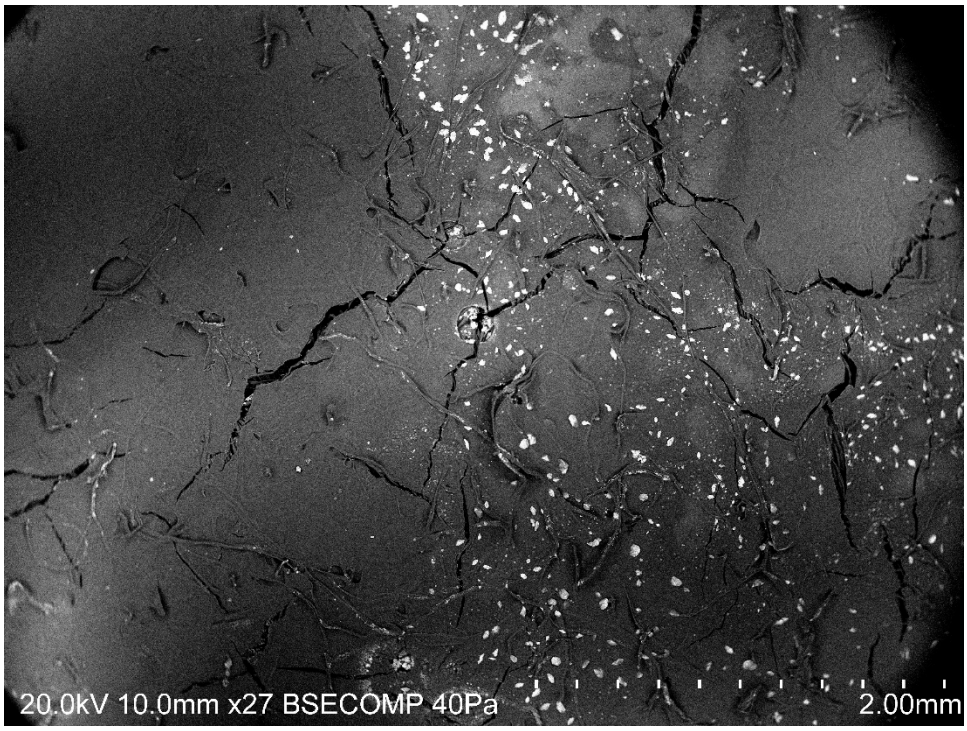


Fig. 3.20. SEM image of Sample ‘C’ at the interface where the gel treated side (left half of image) meets the untreated side (right half of image).

As mentioned earlier in the methodology section of chapter 2, almost all of the treated samples were only treated on one half of the canvas surface which would allow for easier viewing/understanding of the difference between a canvas mock-up treated with a gel vs one that hadn’t undergone any surface treatment. Such is the case in sample ‘C’ (see fig. 3.20) where the SEM image shows the juncture in which the gel treated side (on the left) meets the untreated side (on the right). The salts (which are majority calcium sulfates) are noted in the image by the bright white spots/dots most of which are concentrated on the right half of the image on the untreated side. Some salts do still persist on the treated side, but they are very few

in comparison and for the most part the canvas appears salt-free. This is also corroborated by the SEM mapping image (see fig 3.21) taken at the same interface.

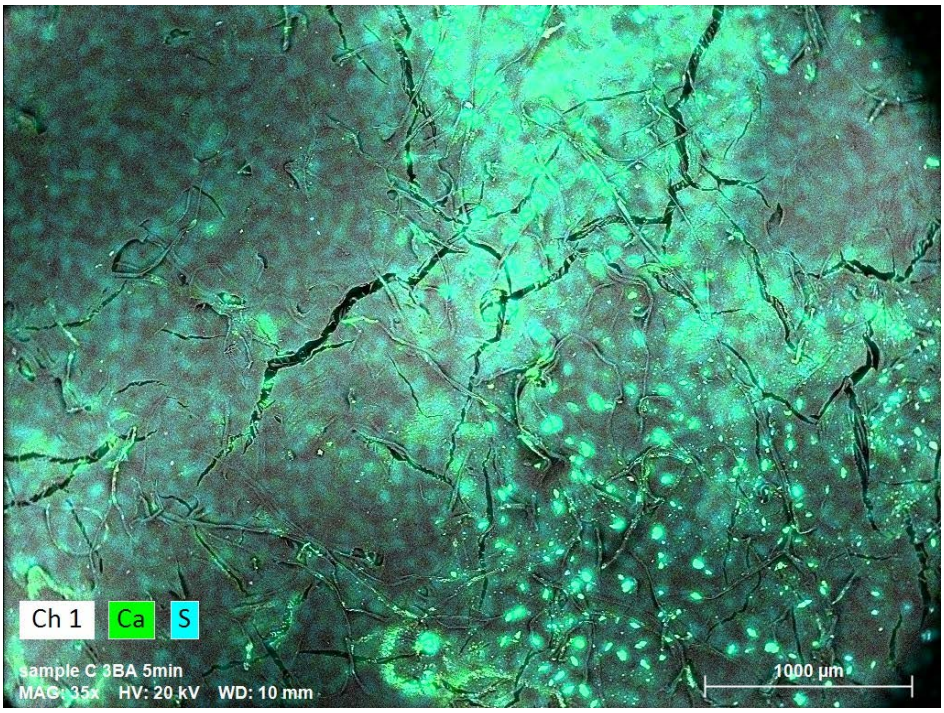


Fig. 3.21. SEM mapping image of the interface, gel treated side (left half) meets the untreated side (right half), blue-green bright spots are the salts.

In the SEM mapping fig. 3.21 it is once again clear that the majority of the salts (noted by blue-green spots) that remain on the mock-up canvas surface are on the untreated side, whereas the treated side shows relatively few salts. This clarity in the interface where the gel treated side presents with relatively few salts and the untreated side with the majority of the salts reside is a reoccurring theme in almost all samples regardless of the treatment time.

Sample ‘F’ – 3% agarose isopropanol gel…

Sample ‘F’ also shows a clear distinction between the gel treated side and the untreated side of the mock-up surface (see fig. 3.22).

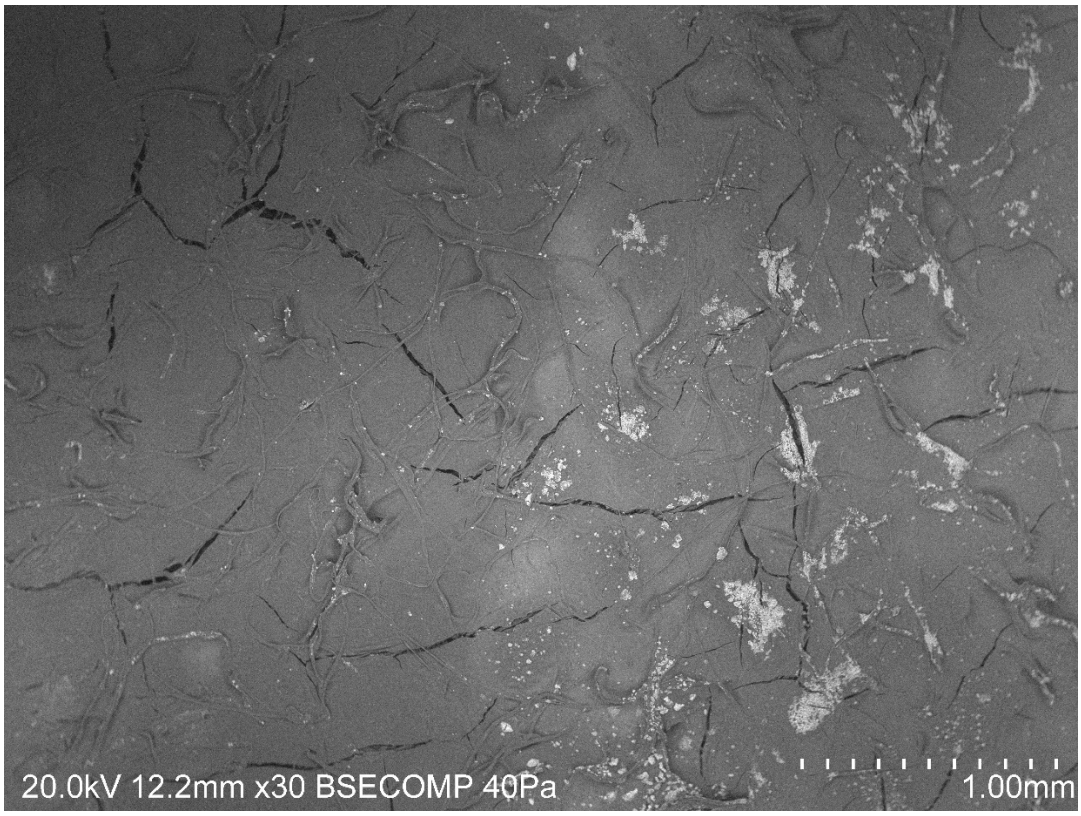


Fig. 3.22. SEM image of sample ‘F’, at the interface of the gel treated side (left) and the untreated side (right).

The gel treated side presents with little to no salts, whereas the untreated side is covered in salts (white patches).

The SEM mapping (see fig 3.23) also confirms the same, the gel treated side of the mock-up presents with almost no salts at all whereas the untreated side is rife with salts.

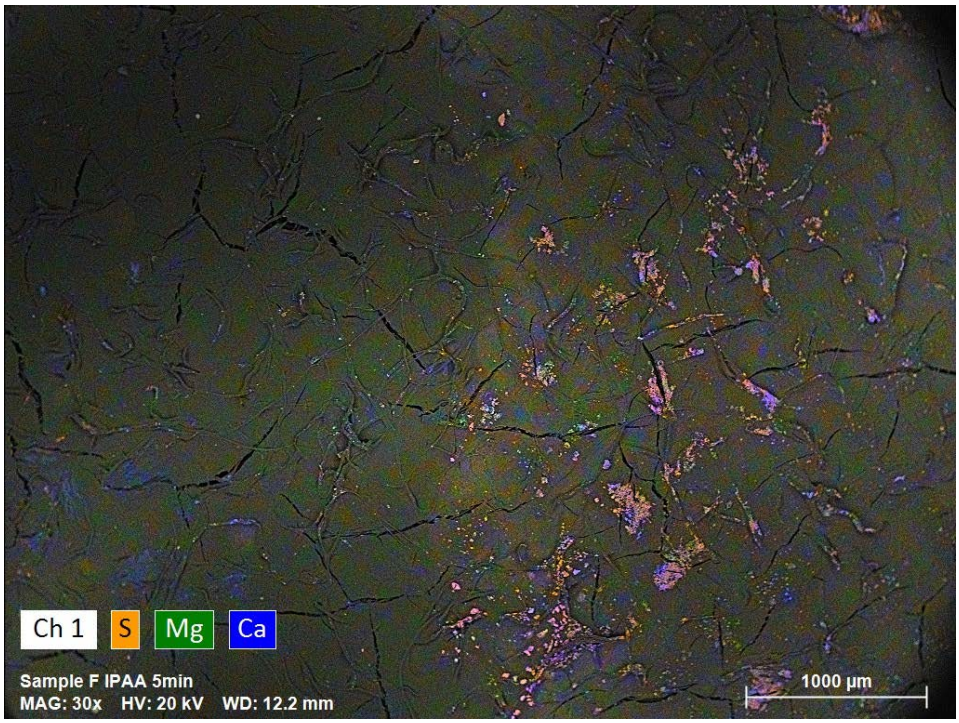


Fig. 3.23. SEM mapping of sample ‘F’, the salts are noted on the untreated side (right) by the elements and their respective colour and intensity.

HIROX images of both treated and untreated side provide the same information as well (see fig 3.24 & 3.25).

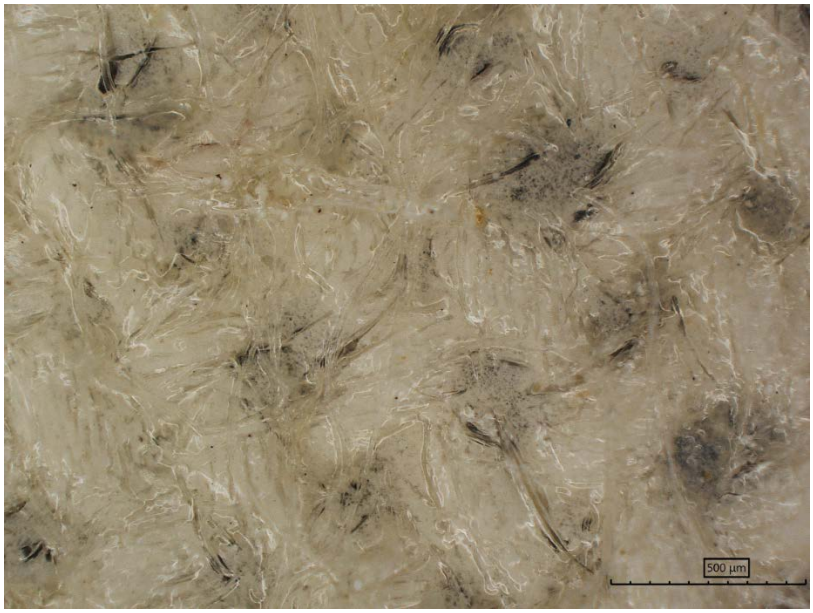


Fig. 3.24. HIROX image (140x mag.) of the gel treated side of sample ‘F’.

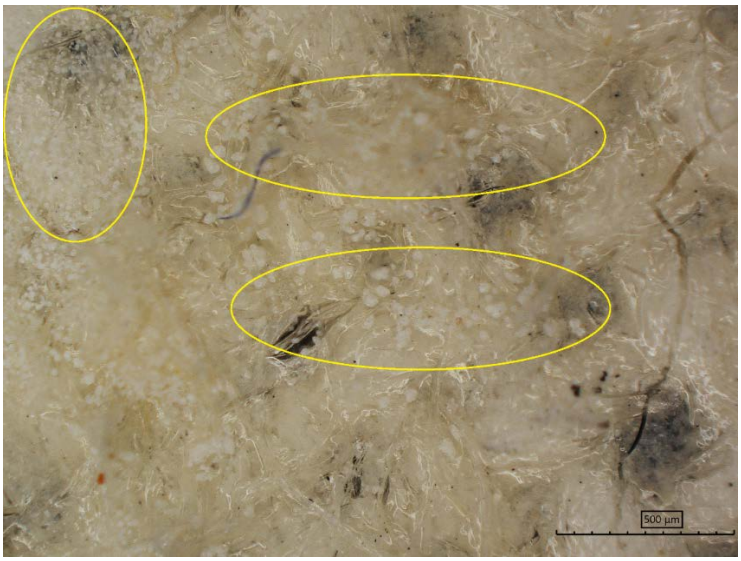


Fig. 3.25. HIROX image (140x mag.) of the untreated side of sample ‘F’, note the large number of salts present throughout the surface.

Sample ‘I’ – 5min…

The 2% agarose acetone gel makes a visible change to the treated areas, although it cannot be said that it removes the salts with the same efficiency as either the 3% agarose butanol gel or the 3% agarose isopropanol gel (see fig. 3.26).

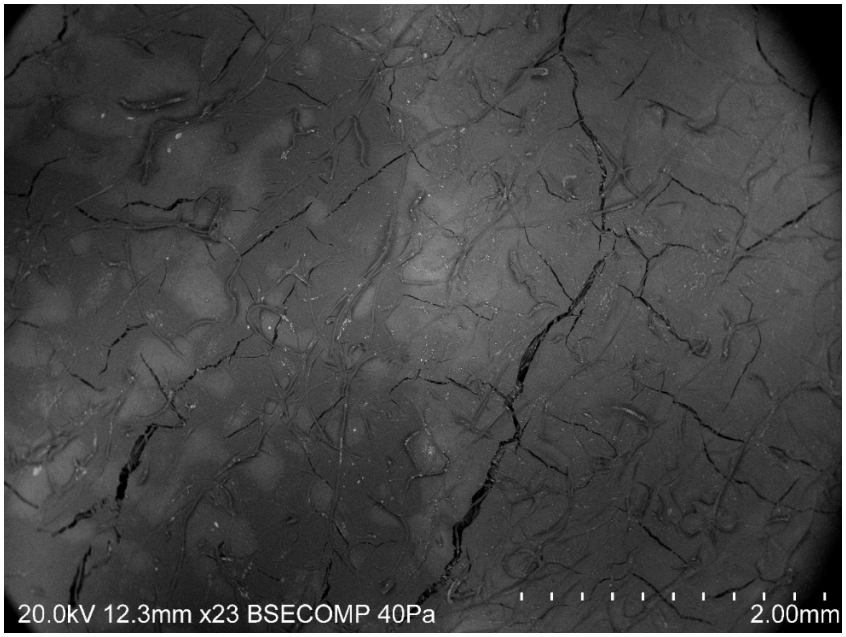


Fig. 3.26. SEM image of Sample ‘I’, where the treated side (left) meets the untreated side (right).

Under SEM imaging of all the analyzed samples, in general the elements (Mg, Ca, and S) appear as a light grey colour and when the colour tends towards very light grey or white (or overexposed) the presence of either magnesium or calcium sulfates are noted. In fig. 3.34 the treated side (left) is generally a dark grey colour due to the more organic nature of the surface (cotton canvas with a layer of dolomitic lime and casein) or in other words due to the lack of elements Mg, Ca, and S. However, many odd-shaped light grey patches (indicating the presence of Mg, Ca and S) can still be noted. The 2% agarose acetone treatment does work to an extent and this can be seen in the results obtained from the area scans of both the treated and untreated sides of the mock-up (see fig. 3.27 and table 3.5).

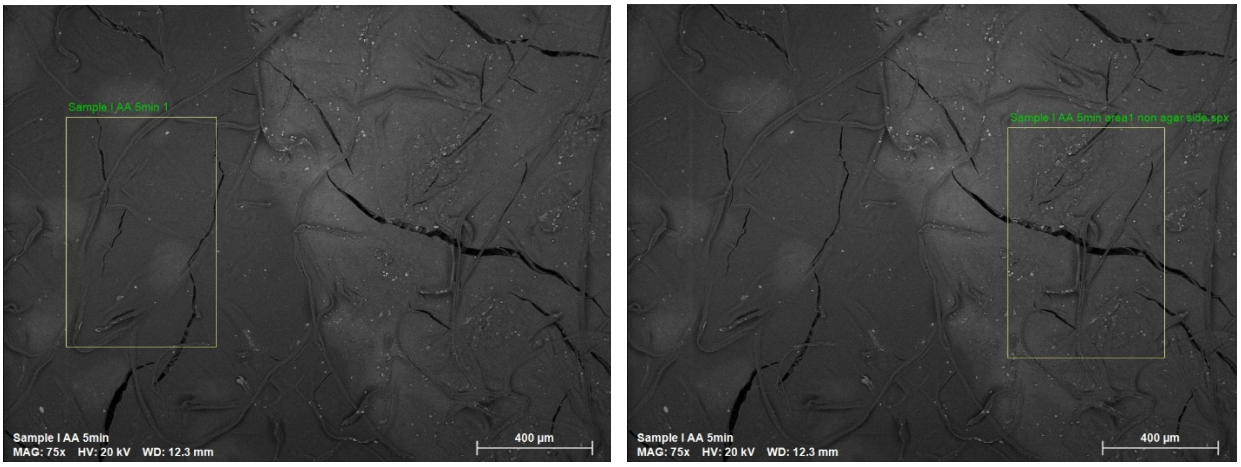


Fig. 3.27. SEM image of area scans (indicated by the yellow box) of the gel treated side (left) and the untreated side (right).

Table 3.5. Sample 'I' area scan results of gel treated side (left) and untreated side (right).

Sample I AA 5min 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	25644	16.74	74.06	84.88
S	16	13544	2.02	8.93	5.10
Ca	20	6267	1.55	6.86	3.14
Mg	12	8097	1.52	6.71	5.06
K	19	2046	0.41	1.82	0.85
P	15	2454	0.37	1.63	0.96
		Sum	**22.60**	**100.00**	**100.00**

Sample I AA 5min 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	24756	28.41	66.26	80.82
Ca	20	22779	6.24	14.56	7.09
S	16	28676	4.60	10.72	6.53
Mg	12	7367	1.56	3.63	2.92
K	19	5748	1.29	3.01	1.50
P	15	4787	0.78	1.82	1.15
		Sum	**42.88**	**100.00**	**100.00**

Note in table 3.5 the quantification of the elements S, Ca, and Mg from the gel treated area scans (left) are overall comparably lower than the untreated side.

Summary of 5min agarose gel treatments

From the information gathered by the SEM-EDS and XRD analysis of all 5min loaded agarose gel treated samples. It is clear that sample 'C' treated with a 3% agarose butanol gel shows the best results in terms of efficiency in salt-removal. While both sample 'F' and 'I' treated with a 3% agarose IPA gel and a 2% agarose acetone gel respectively, performed similarly to each other and poorly compared the 3% agarose butanol gel.

3.3.2.2. Gels Applied for 1 hour…

Sample 'D' – 3% butanol agarose gel…

Sample 'D' was treated for 1h with a 3% agarose butanol gel. There is a clear difference between the gel treated and untreated side (see fig 3.28).

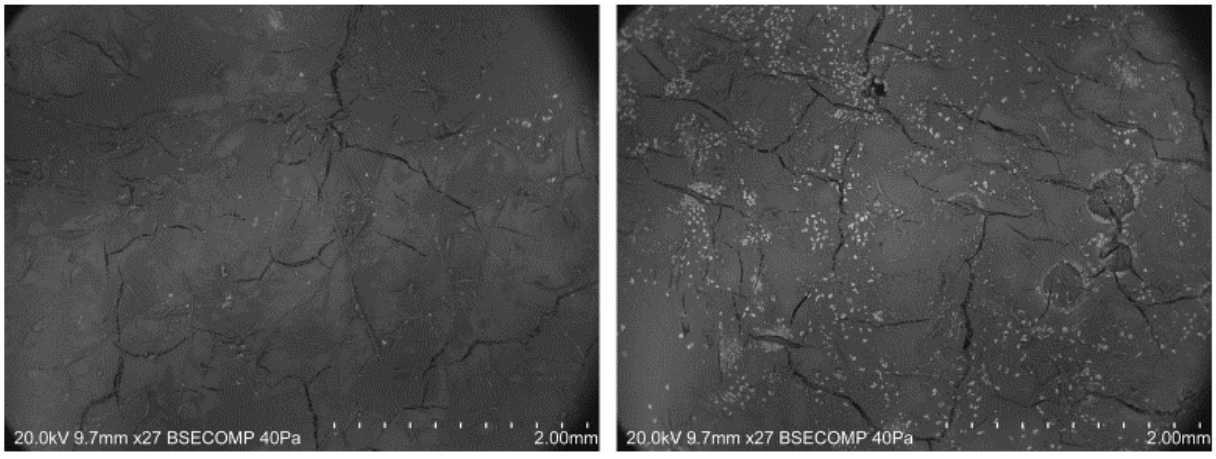


Fig. 3.28. SEM images of sample 'D', on the treated side (left) very few salts present, while the majority of the salts (small white spots) are present on the untreated area (right).

Sample ‘G’ – 3% agarose isopropanol gel…

Concerning the cleaning efficiency of the 3% agarose IPA gel treatment of sample ‘G’, the results were quite similar to sample ‘F’, wherein the treated side of the sample was very clearly lacking of salts while the untreated side was quite full of them. Of note in sample ‘G’ for the first time was the presence of magnesium sulfates (see fig. 3.29) which have been the minority when compared to the presence of calcium sulfates. A rough estimate would be that approximately 10% of all salts present between all analyzed samples are magnesium sulfates, the rest being calcium sulfates in many different structural formations.

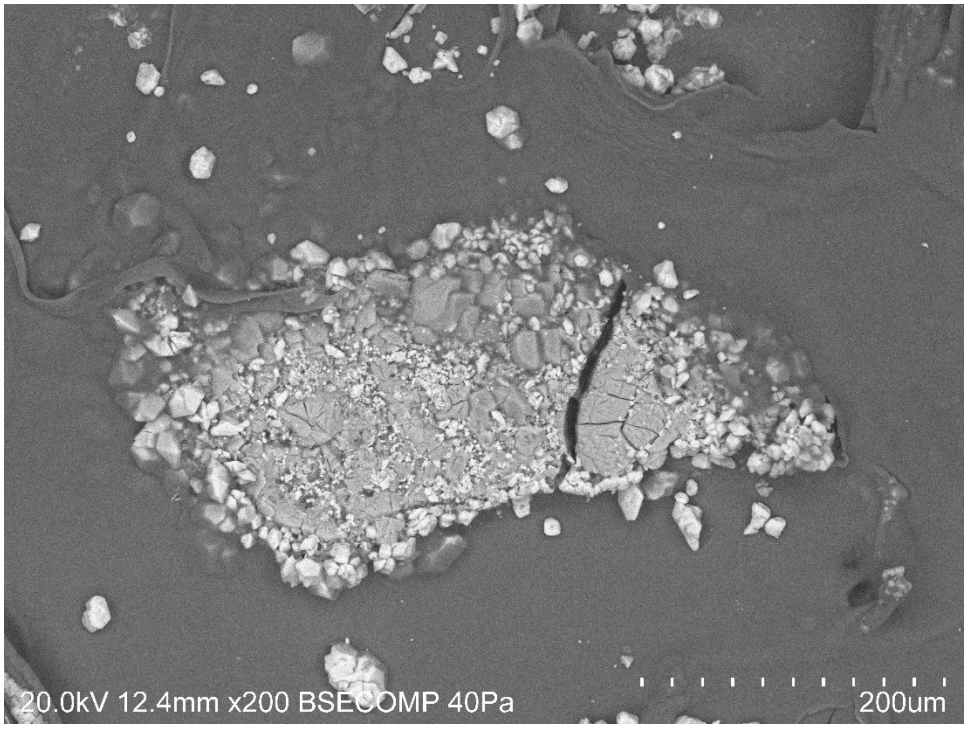


Fig. 3.29. SEM image of sample ‘G’, magnesium sulfates in the center surrounded by the (whiter) calcium sulfates.

Whenever magnesium sulfates were noted on any sample, whether on the treated or the untreated surface, they were often also surrounded by calcium sulfates

too. SEM mapping (see fig. 3.30) of the same salt (as above) shows this phenomenon quite well.

Fig. 3.30. SEM mapping image of the salts by their elements, Mg (yellow) in the center flanked on all sides by Ca (orange).

Table 3.6. SEM point analysis from the center of the salts from fig. 3.30, note the overwhelming amount of element Mg as compared to Ca.

Sample G IPAA 1hr 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
O	8	20920	37.11	46.30	60.93	1.88	5.05
S	16	88145	21.96	27.39	17.99	0.70	3.19
Mg	12	44183	17.05	21.28	18.43	0.92	5.38
Ca	20	10636	4.04	5.04	2.65	0.13	3.24
		Sum	**80.16**	**100.00**	**100.00**		

Sample 'J' – 2% agarose acetone gel…

The treatment of sample 'J' with a 2% agarose acetone gel for the duration of 1h presents a similar efficiency in salt removal as that of the same gel treated for 5min on sample 'I'. This indicates that cleaning efficiency of this particular gel with this particular formulation is not greatly impacted by the treatment duration.

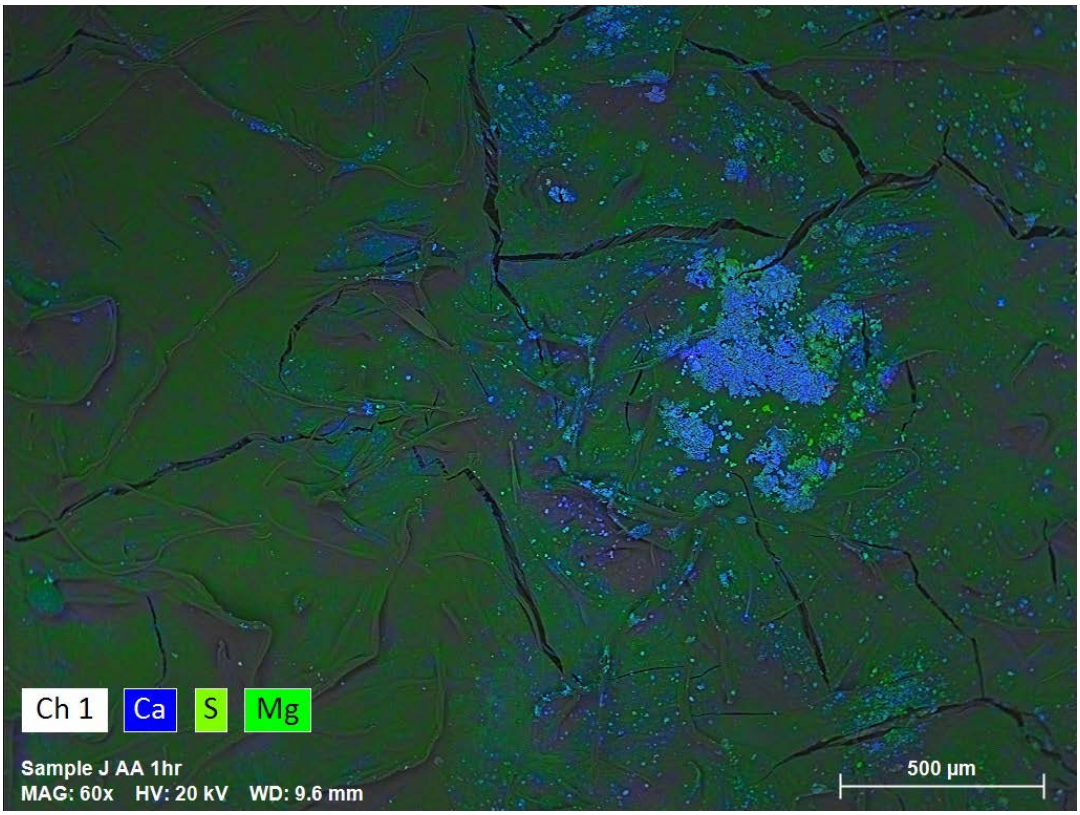


Fig. 3.31. SEM mapping image of sample 'J', at the interface of the gel treated side (left) and the untreated side (right), showing the elements Ca, S, and Mg.

In fig. 3.31. it is clear that the gel(s) are efficient in the removal of crystalline formations of both calcium and magnesium sulfates (or carbonates). Note that in the same image on the gel treated side, although the element Mg is present, it does not equate to the presence of any magnesium sulfates.

Summary of 1 hour agarose gel treatment…

From the analysis of the 1h agarose gel treated samples it can be concluded that all formulations of gels tested in this category perform very well and similarly to each other in the removal of salts. The differences in the percentages of gels or in the cleaning solutions used did not make a noticeable difference in the salt-removal efficiency, and nor did any gel cause structural / surface damage.

3.3.2.3. Gels Applied for 3 days…

Sample 'E' – 3% agarose butanol gel…

The entire surface of the canvas of sample 'E' was covered with a 3% butanol agarose gel for approximately 72h. The vastly increased duration of the treatment of the sample did not result in a proportionate decrease in salts. As (fig 3.32) shows, although the majority of the canvas is clean, some salts do remain, and the majority of the salts that do remain, are in clusters or in a ring-like formation (see fig. 3.33).

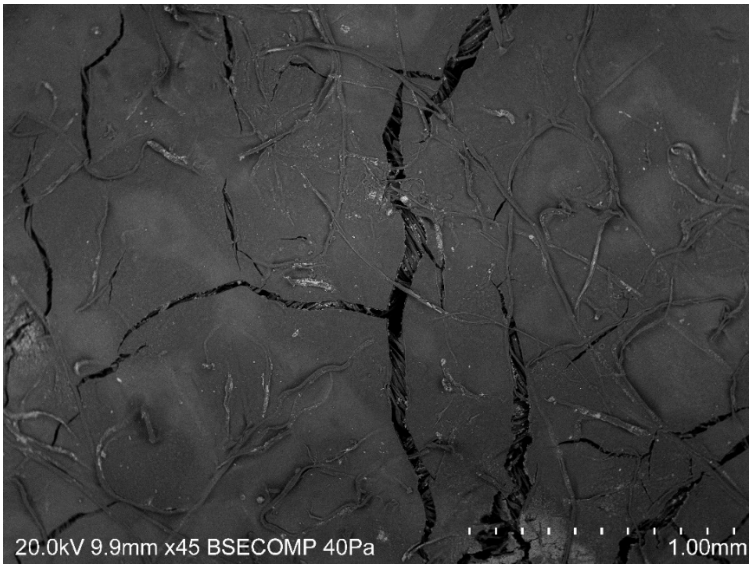


Fig. 3.32. SEM image of sample 'E', mostly a clean canvas excepting for the white streaks and spots that are salts.

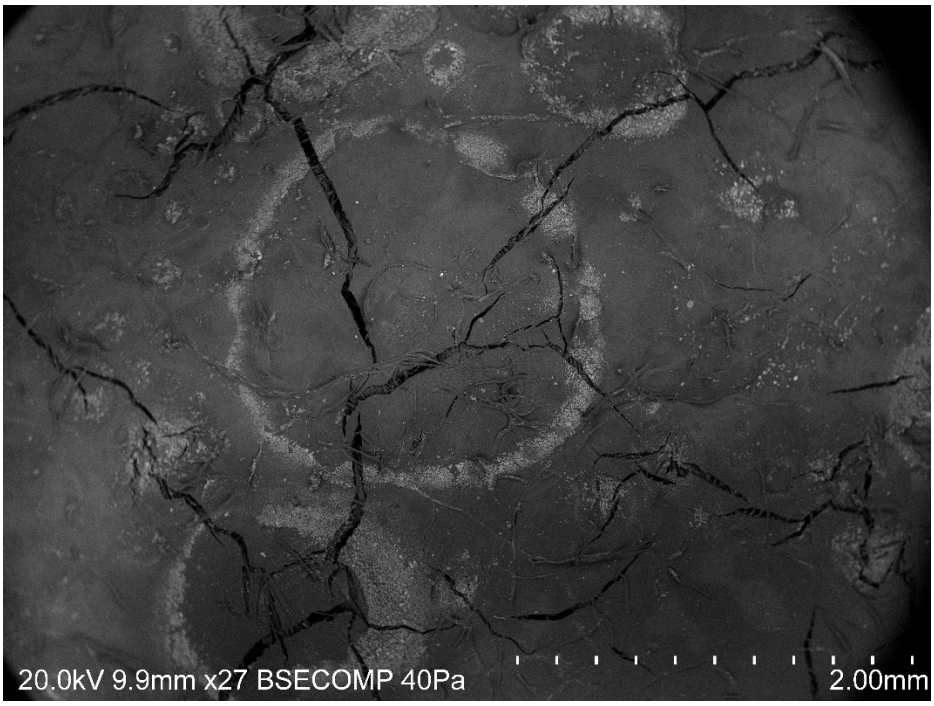


Fig. 3.33. SEM image of sample ‘E’, showing ring-like formation of salts (mostly calcium sulfates).

Sample ‘E’ also exhibited a very prominent yellow tinge across almost the whole sample surface after having been treated. The pure unbleached cotton canvas was already of a light yellow colour, but sample ‘E’ was most certainly, visibly (to the naked eye) much yellower than any other treated sample (see fig. 3.34).

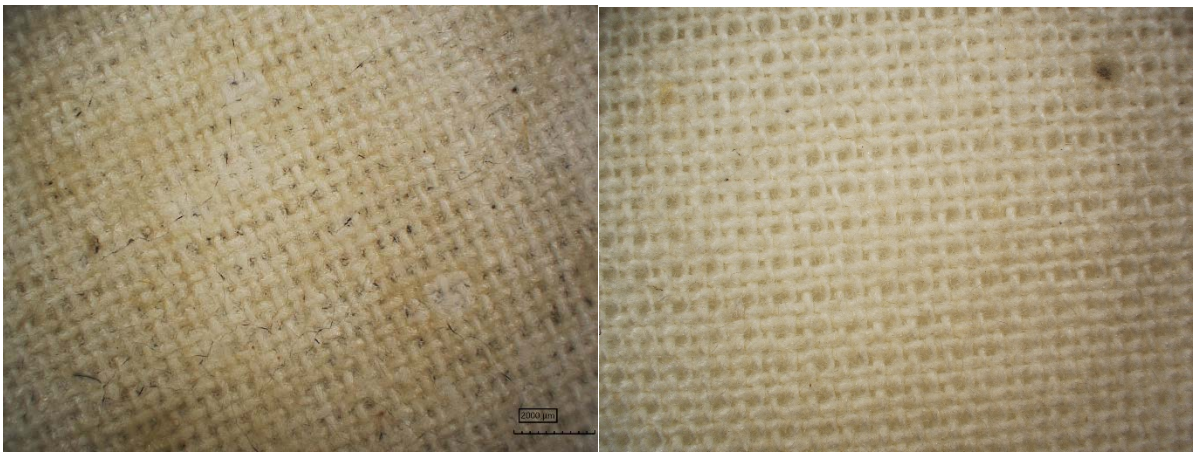


Fig. 3.34. HIROX images (20x mag.) of sample ‘E’ (left) with excessive yellowing, vs the “normal” colour of a sample surface (right).

Sample ‘E’ also presented with a foul odor many days after being treated. Owing to the fact that this sample was treated for 3 days with an agarose gel that would have kept the sample wet for the entire duration, and also since agarose is a key component in the cultivation of bacteria, it is highly likely that both the surface staining and the foul odor is a direct result of the extended duration wherein the sample was either wet or damp and a result of the bacteria that must have grown in these conditions. Although no compromise in the structural integrity of the canvas was noted under any magnification in SEM as a direct result of the treatment, aesthetically there was certain compromise.

Sample ‘H’ – 3% agarose isopropanol gel…

Sample ‘H’ was treated with a 3% agarose IPA gel for 3 days, and as mentioned earlier in chapter 2, it was the only sample where the agarose gel was “poured” over the entire mock-up in a semi solid state in order to achieve optimum contact with the canvas surface (refer fig. 2.7 & fig. 2.8). Although great contact was achieved between gel and surface, and the salts were removed with similar efficiency to that of the two other 3% agarose IPA gel treated samples (‘F’ & ‘G’), growth of mold/fungi (see fig. 3.35) was noted on a small area (<1cm^2) of the surface most likely caused by the lengthy exposure to the gel i.e., wet/damp conditions.

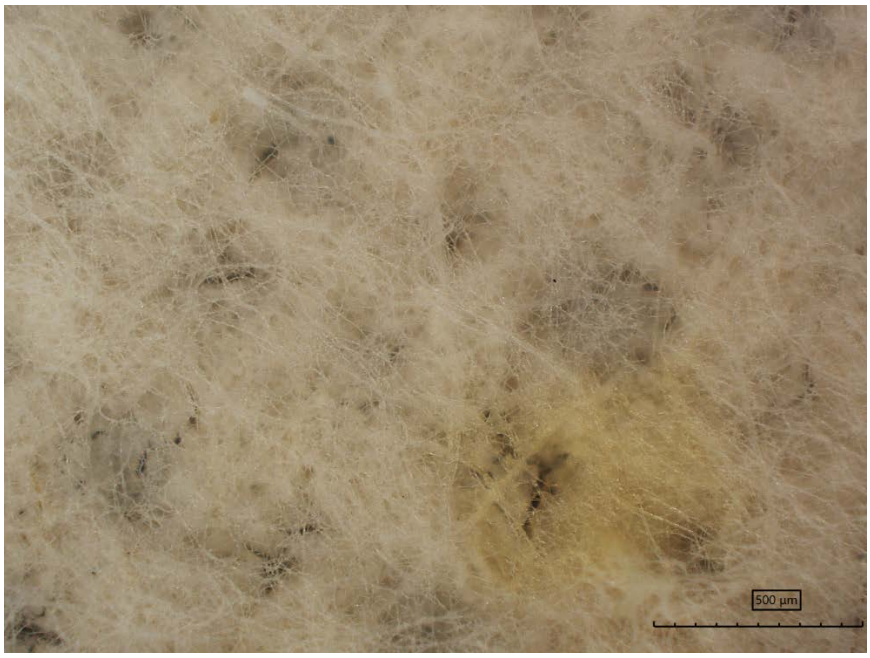


Fig. 3.35. HIROX image of sample ‘H’ showing the coverage of the mold over the canvas.

SEM imaging of the mold area showed the presence of salts embedded within the mold structure (see fig 3.36).

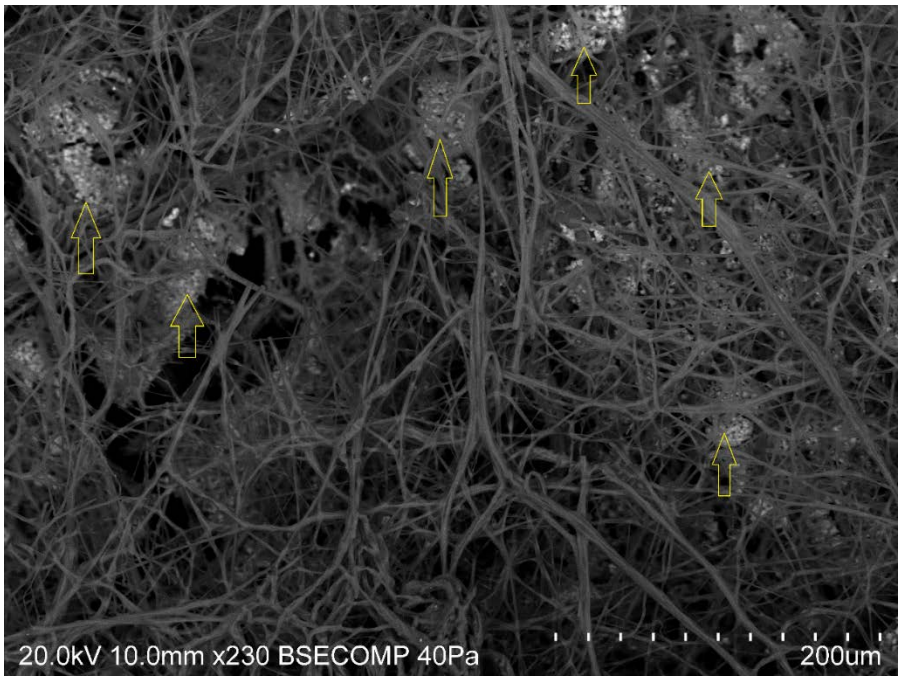


Fig. 3.36. SEM image of the mold/fungi structure within which the salts (yellow arrows) are embedded.

Although the sample surface was cleaned of salts with good efficiency, the growth of mold/fungi is neither desirable nor an ideal outcome to the structural integrity of the sample surface.

Sample 'K' – 2% agarose acetone gel…

Not much can be said about the efficiency of the gel in the removing of salts from sample 'K', as the entirety of the treated side of the sample mock-up has been heavily deteriorated by the 2% agarose acetone gel (see fig. 3.37) which indicates no possible compatibility of the formulation for the gel used.

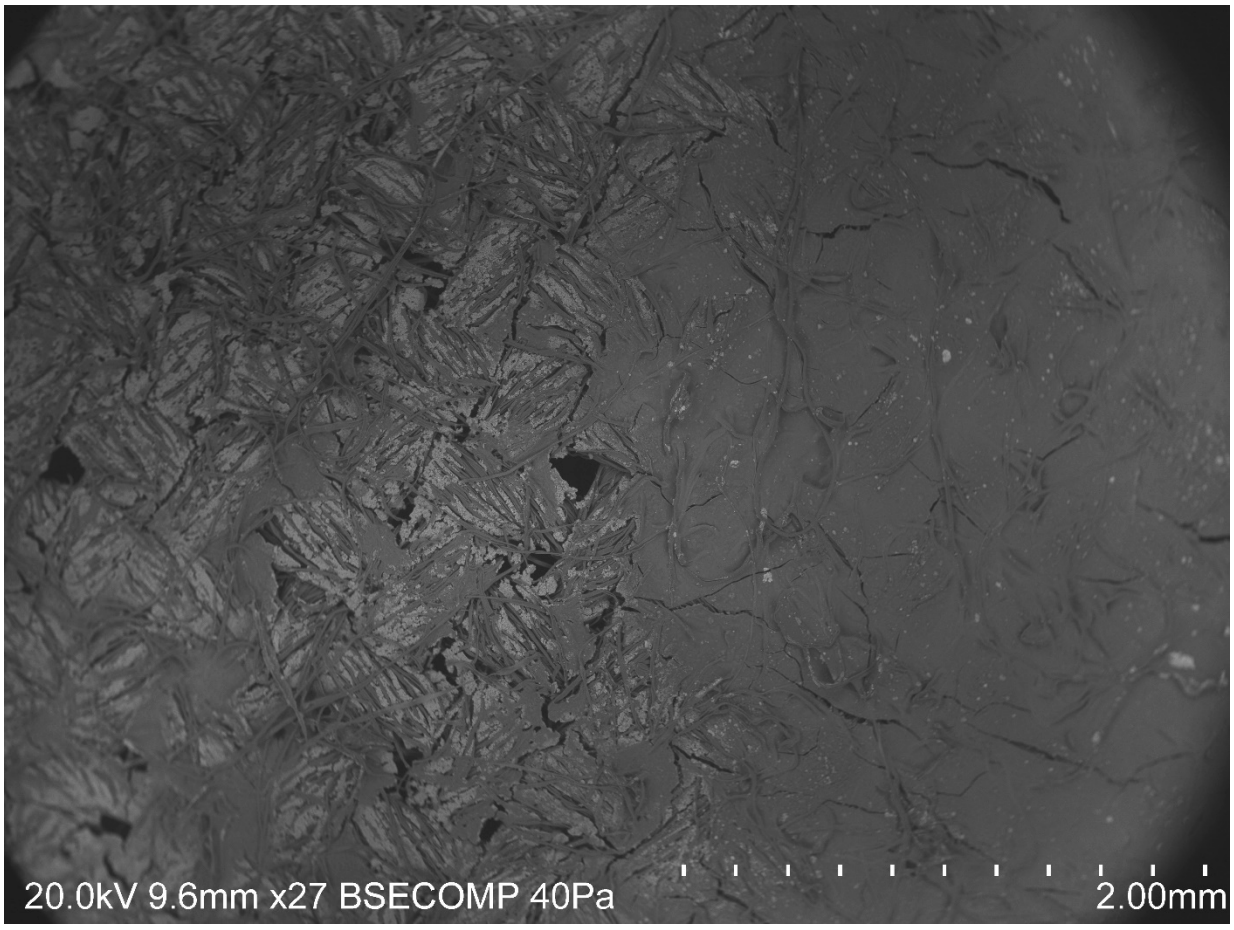


Fig. 3.37. SEM image of sample 'K', at the interface, gel treated side (left) and untreated side (right). Note the extensive surface deterioration on the treated side.

It is very apparent from fig. 3.37 that an agarose gel loaded with a 10% acetone solution is not suitable for a treatment duration of 3 days. Sample ‘I’ and sample ‘J’ were treated with the same 2% agarose acetone gel for 5min and 1h respectively and they do not seem to present any apparent structural damage to the sample surface. Whereas, the gel treated side of sample ‘K’ presents extensive surface damage in the form of large cracks and holes, and the chemical erosion of both the dolomitic casein layer and the cotton canvas underneath. Furthermore, counterintuitively the gel treated side presents with the majority concentration of the element Ca (and a small concentration of Mg), whilst the untreated side only presents with the elements Mg and S (see fig. 3.38).

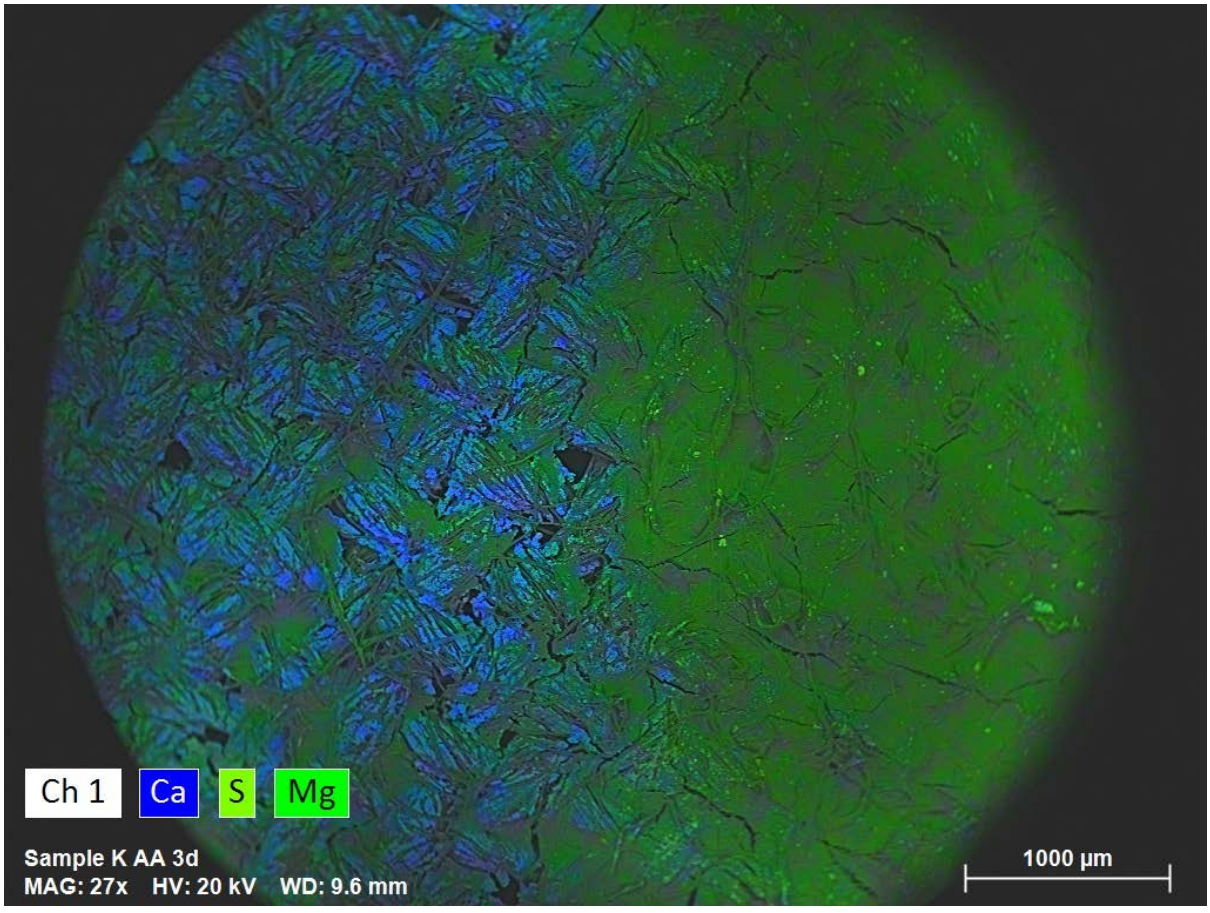


Fig. 3.38. SEM mapping image of sample ‘K’, gel treated side (left) with mostly Ca and untreated side (right) with most Mg and S.

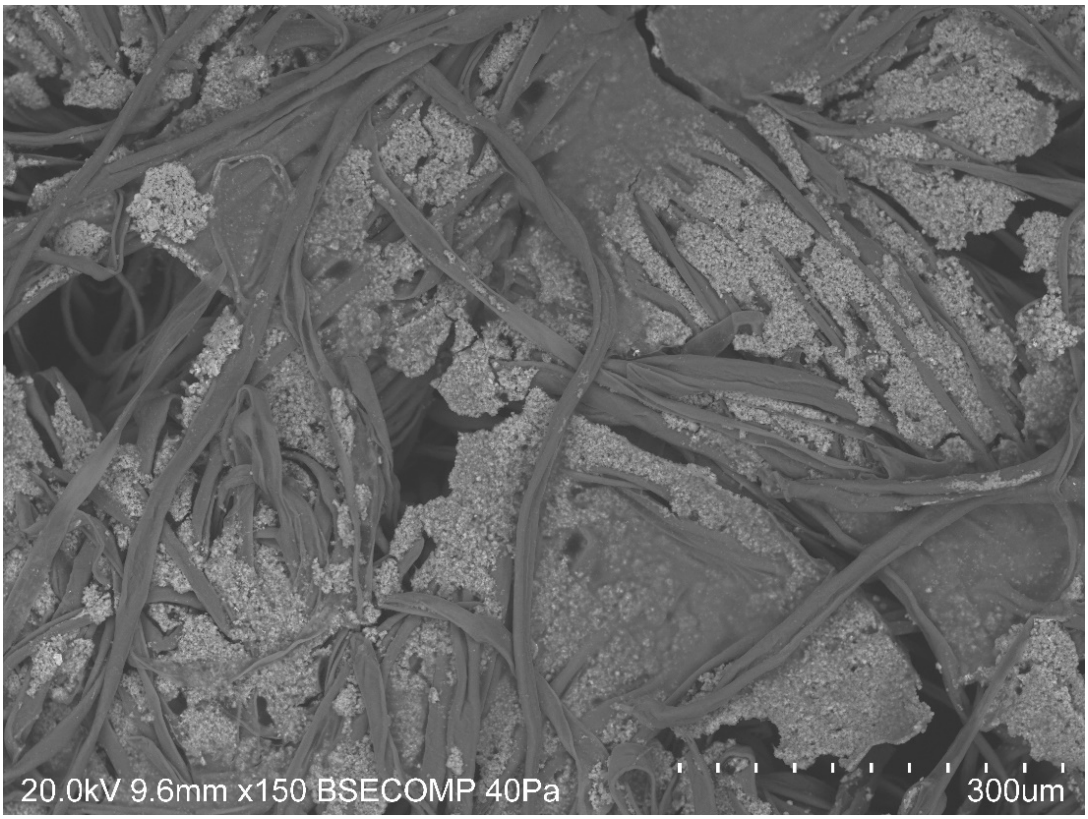


Fig. 3.39. SEM image of sample ‘K’, a closer look at the surface deterioration.

It is perhaps, of no surprise to anyone that a “harsh” chemical such as acetone exposed to a surface such as of the sample mock-up for an extended period can cause as much damage as it has. And though this extended period of exposure of the mock-up surface to the gel did not result in any mold/fungi formation unlike sample ‘H’, the surface damage is enough to conclude that the structural integrity of the mock-up has been heavily compromised and that an acetone loaded gel is definitely not suitable for an extended duration of application nor perhaps even for short durations as they are seemingly less efficient at salt removal than butanol and isopropanol loaded agarose gels.

Summary of 3-day agarose gel treatment…

The results of all 3 agarose gel treatments were extremely varied. The 3% agarose butanol gel was quite efficient in salt removal, while the 3% agarose IPA gel was excellent at salt removal and lastly the 2% agarose acetone gel was terrible at salt removal and caused immense damage to the treated surface.

3.4. Analysis of Polyacrylamide Gel Treatments by SEM-EDS & XRD…

3.4.1. Unloaded / Plain 5% Polyacrylamide Gel…

Sample 'M' – 5min…

Despite the sample being treated for only 5min with a plain 5% polyacrylamide gel the treated side displays very few salts and the distinction between the treated and untreated side is quite apparent (see fig. 3.40).

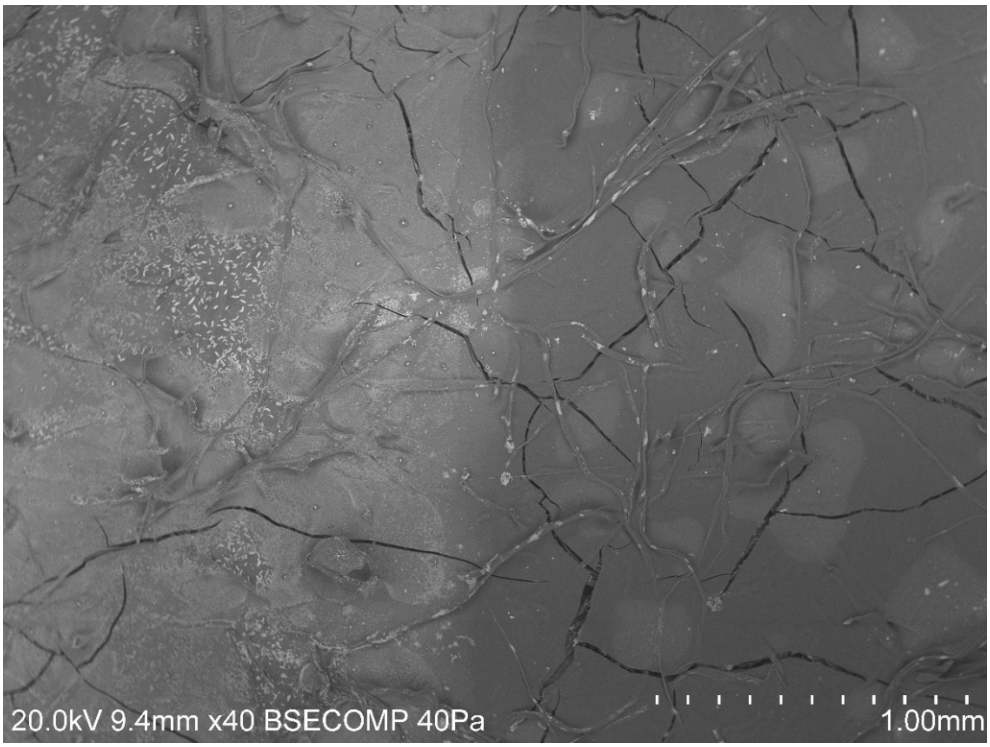


Fig. 3.40. SEM image of sample 'M', untreated side (left) and treated side (right).

The same difference in the presence of salts can be seen from the results of area scans from the treated and untreated side (see fig. 3.41 & table 3.7).

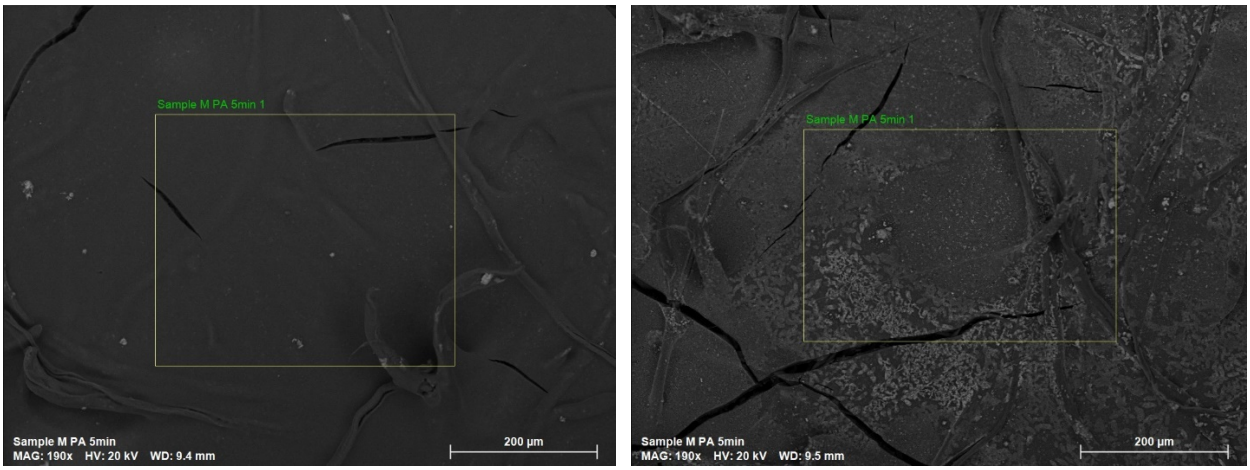


Fig. 3.41. Area scans of sample ‘M’, treated side (left) and untreated side (right).

Table 3.7. Quantification of area scans of sample ‘M’, untreated side (left), gel treated side (right).

Sample M PA 5min 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
C	6	20001	44.62	43.36	54.83
O	8	24736	41.13	39.98	37.95
Mg	12	6118	1.26	1.22	0.76
S	16	39492	5.60	5.44	2.58
K	19	18698	3.44	3.34	1.30
Ca	20	27748	6.18	6.00	2.27
P	15	3663	0.54	0.52	0.26
Cl	17	896	0.14	0.14	0.06
		Sum	**102.90**	**100.00**	**100.00**

Sample M PA 5min 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
C	6	68446	67.59	67.59	74.88
O	8	20792	27.88	27.88	23.19
Mg	12	9068	1.20	1.20	0.66
S	16	18215	1.82	1.82	0.75
Ca	20	7014	1.14	1.14	0.38
P	15	2268	0.23	0.23	0.10
K	19	1007	0.14	0.14	0.05
		Sum	**100.00**	**100.00**	**100.00**

In table 3.7 note the presence of elements Mg, and especially S, and Ca are considerably lower on the treated side when compared to the untreated side.

Sample ‘N’ – 1hr…

Sample ‘N’ was also treated with an unloaded / plain polyacrylamide gel, but, for the duration of 1 hour. The distinction between the treated side and the untreated

side of the sample is not as clear as sample ‘M’ as a large number of salts still remain on the treated side (see fig 3.42).

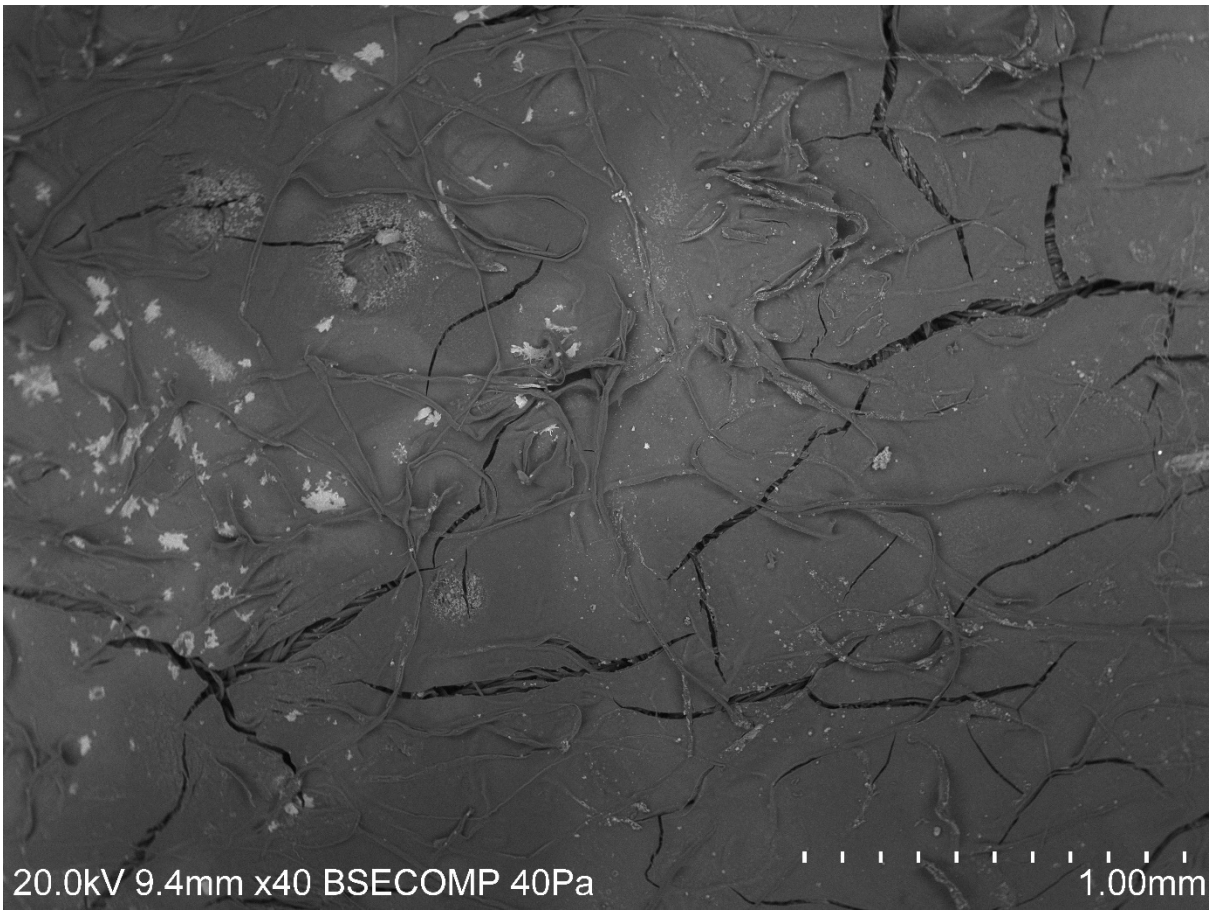


Fig. 3.42. SEM image of sample ‘N’, gel treated side (left) and untreated side (right).

Note the salts (indicated by white spots) in the above figure still present on the treated side (left). The surface of the treated side was heavily cracked and was generally littered with salts in a variety of patterns, mainly in the ring-like formation mentioned earlier (see fig. 3.43). Much of the salts on the treated side were Ca based, however, a large cluster of magnesium sulfates surrounded by smaller formations of calcium sulfates was also noticed on the untreated side of the sample (see fig. 3.44).

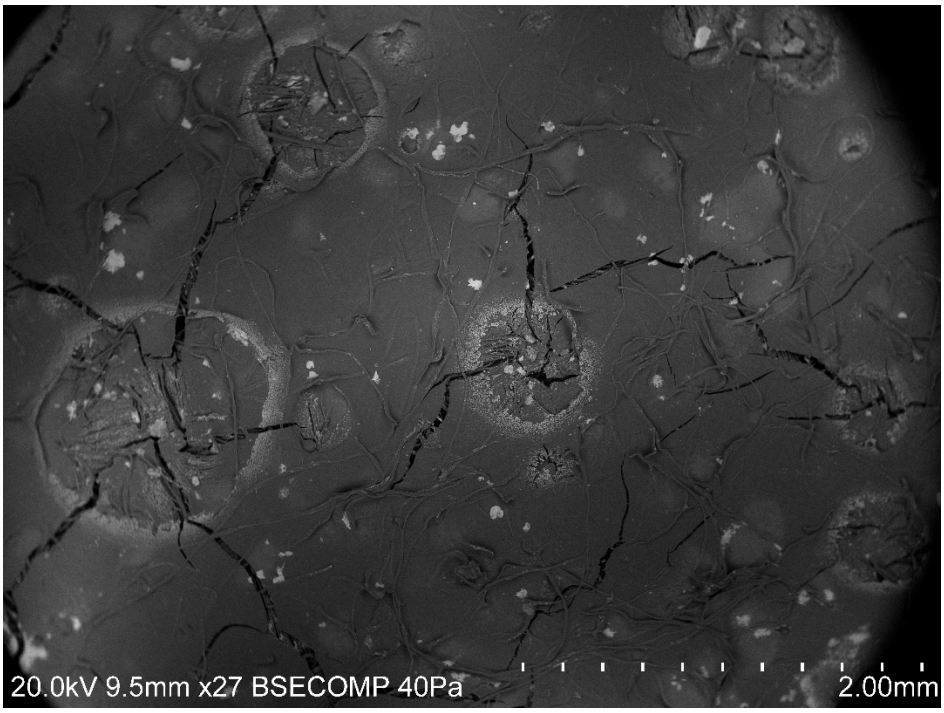


Fig. 3.43. SEM image of sample ‘N’, of the treated side showing great surface cracking and a large number of salts, specifically those that are ring shaped.

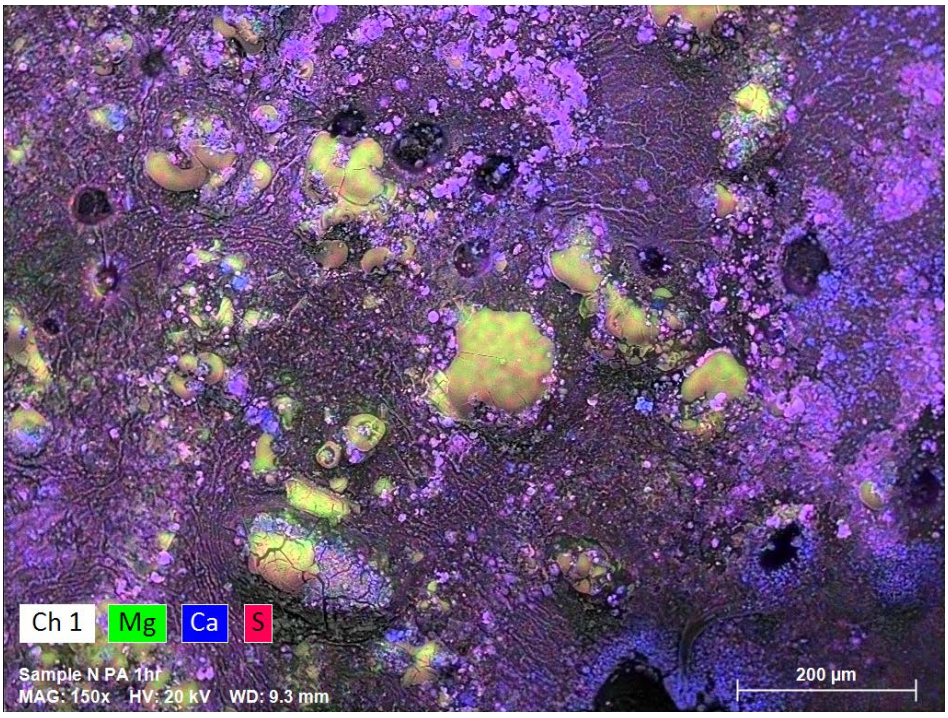


Fig. 3.44. SEM mapping image of sample ‘N’ showing a large cluster of Mg based salts (yellow-green) surrounded by smaller and tightly packed Ca based salts (purple).

Summary of 5min & 1h unloaded polyacrylamide gel treatments…

Two samples (‘M’ & ‘N’) were treated using unloaded/plain 5% polyacrylamide gels, for the duration of 5min and 1h respectively. Both present such varying results that no conclusion can be drawn on the salt removal capabilities / efficiency of a 5% unloaded/plain polyacrylamide gel. Further testing is required in this aspect.

3.4.2. Loaded Polyacrylamide gels…

5% polyacrylamide gels were made, loaded with butanol, isopropanol and acetone and tested on samples ‘O’ through ‘K’. following are their results:

3.4.2.1. Gels Applied for 5 minutes…

Sample ‘O’ – 5% polyacrylamide butanol gel…

On first glance the 5% polyacrylamide butanol gel seems to have removed a good number of salts on the treated side (see fig. 3.45) and the SEM mapping data

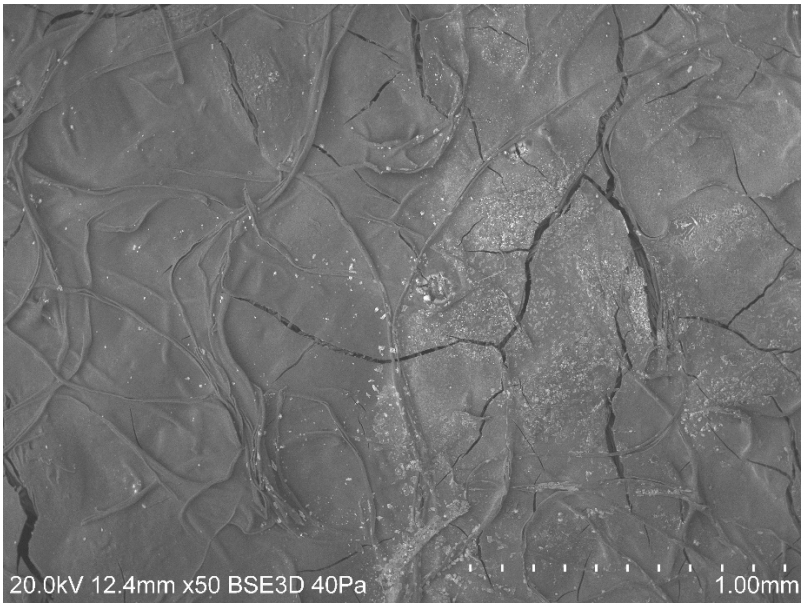


Fig. 3.45. SEM image of sample ‘O’, treated side (left) and untreated side (right).

seems to show the same (see fig. 3.46). however, area scans of the treated and untreated areas show a good reduction in the element Ca, but not so much of the sulfur and an uptick in the element Mg on the treated side (see fig. 3.47 & table 3.8).

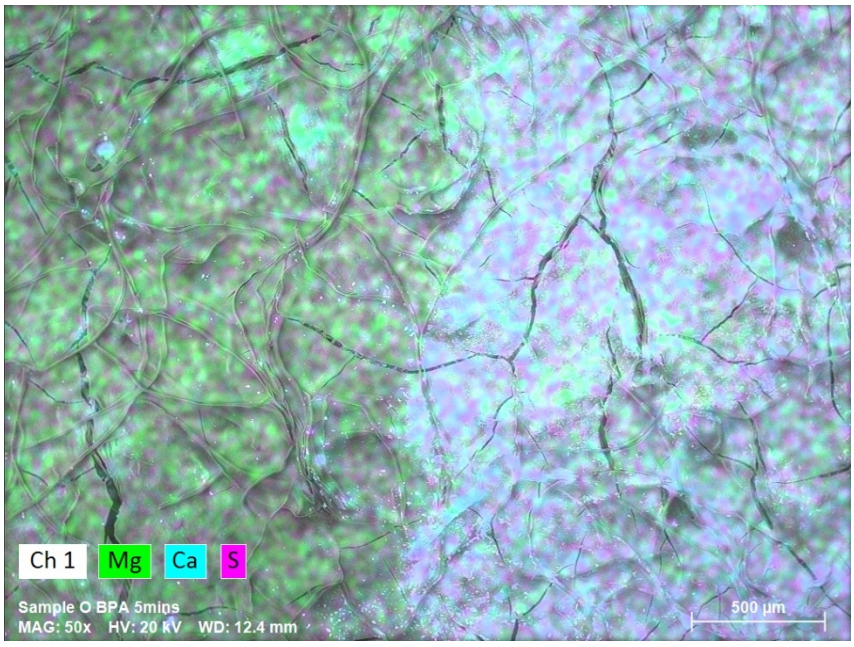


Fig. 3.46. SEM mapping image of the elements Mg, Ca, and S of sample ‘O’, treated side (left) and untreated side (right).

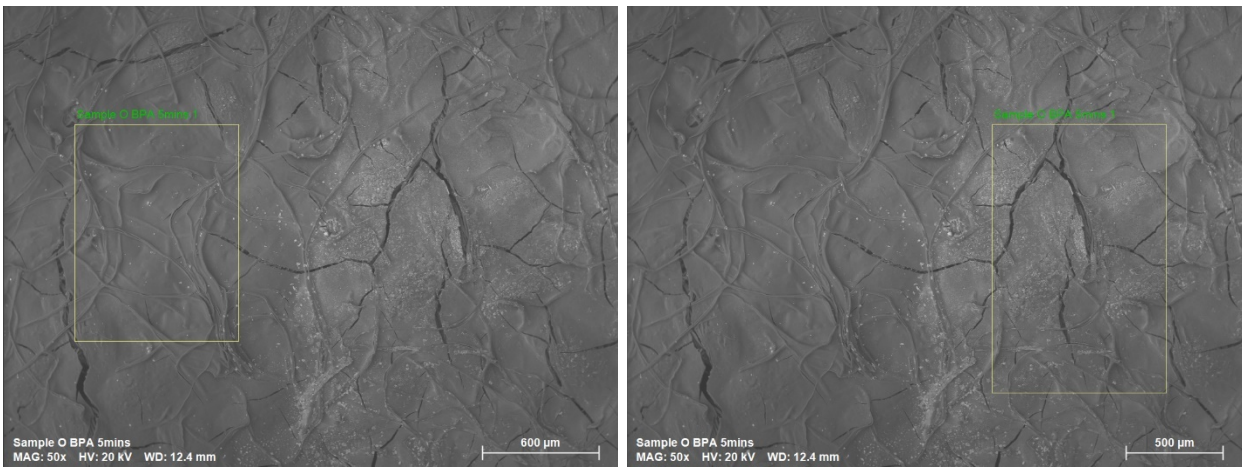


Fig. 3.47. Area scans of sample ‘O’, treated side (left) and untreated side (right).

Table 3.8. Quantification of Area scans of sample ‘O’, treated side (left) and untreated side (right).

Sample O BPA 5mins 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	26958	18.32	72.22	83.55
S	16	18520	2.75	10.84	6.26
Mg	12	9244	1.80	7.10	5.40
Ca	20	6940	1.66	6.54	3.02
P	15	2801	0.42	1.67	1.00
K	19	2079	0.41	1.63	0.77
		Sum	**25.37**	**100.00**	**100.00**

Sample O BPA 5mins 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	28365	33.88	65.60	80.35
Ca	20	25350	7.14	13.82	6.76
S	16	36657	5.86	11.35	6.94
K	19	9307	2.14	4.14	2.08
Mg	12	8654	1.98	3.84	3.10
P	15	3919	0.64	1.24	0.79
		Sum	**51.65**	**100.00**	**100.00**

In general, on the gel treated side of sample ‘O’, large sections where salts were present (mainly calcium sulfates) was noted (see fig 3.48).

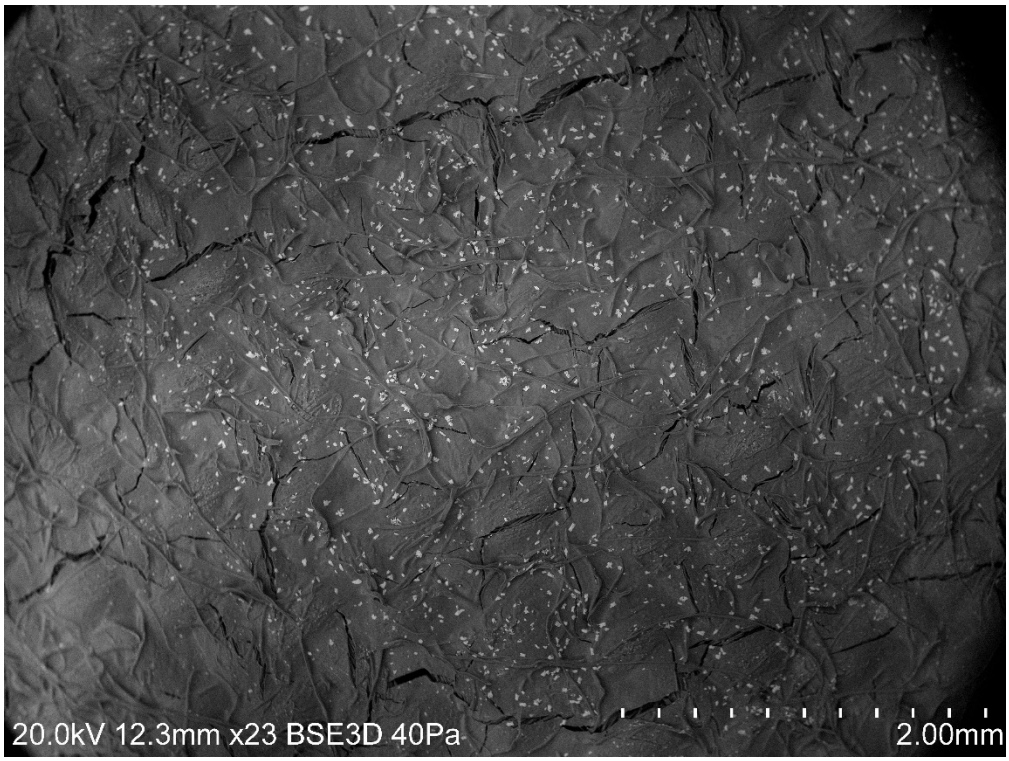


Fig. 3.48. SEM image of treated side of sample ‘O’ showing the presence of a large scattering of calcium sulfates.

Sample ‘R’ – 5% Polyacrylamide IPA gel…

There is a clear visual difference between the treated and untreated side of sample ‘R’, and although the treated side of the sample was generally lacking of salts, however, it was not completely salt-free (see fig. 3.49 & fig. 3.50).

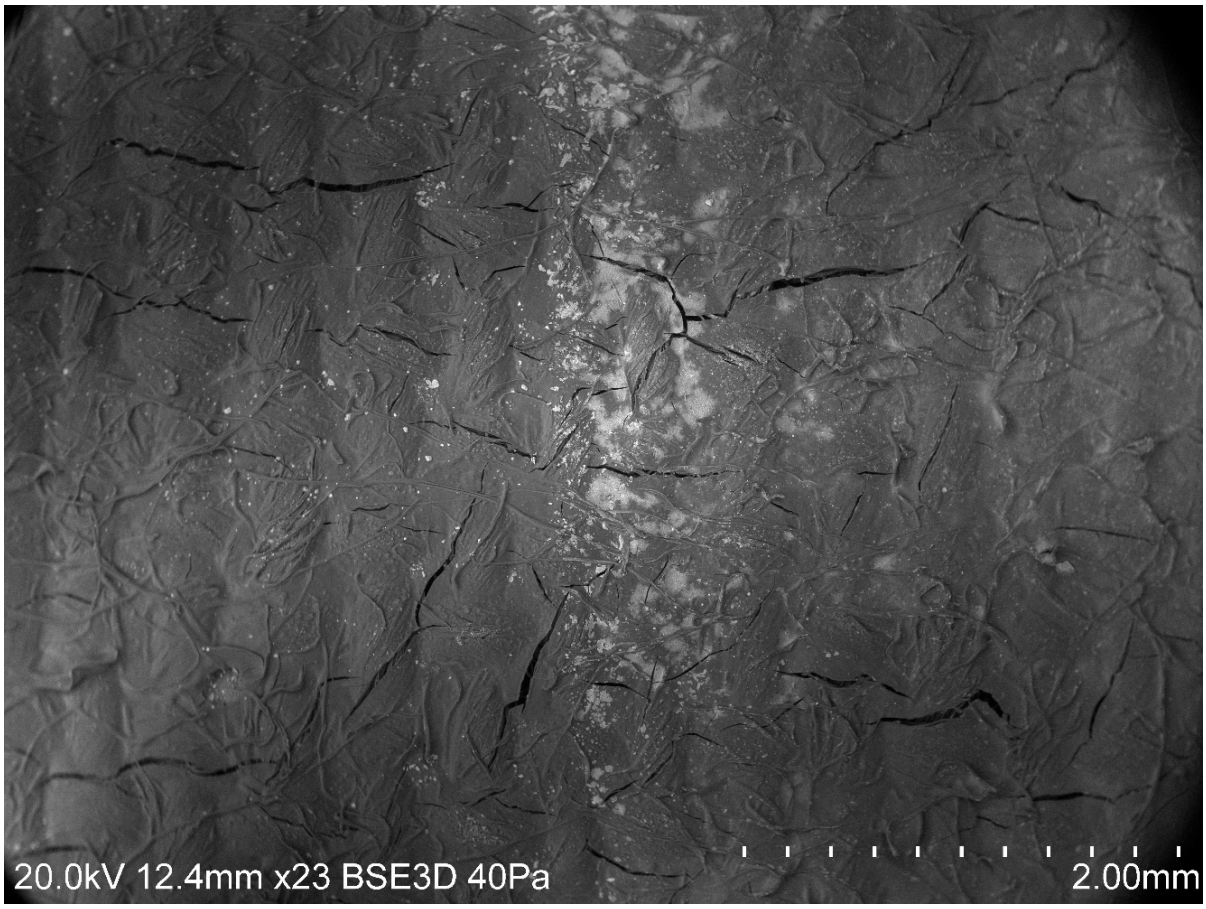


Fig. 3.49. SEM image of sample ‘R’, at the interface, showing a clear difference in the treated side (left) and untreated side (right).

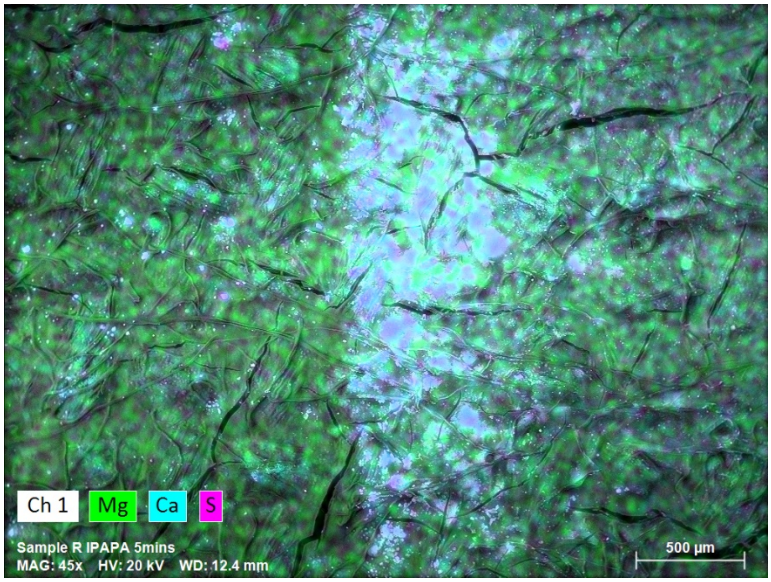


Fig. 3.50. SEM mapping image of elements Mg, Ca, and S, on sample ‘R’.

Sample ‘U’ – 5% Polyacrylamide acetone gel…

The 5% polyacrylamide acetone gel has removed some salts on the treated surface but a large quantity of salts still remains on both the treated and untreated side of the sample (see fig. 3.51). SEM imaging revealed that sample ‘U’ had the absolute greatest number of salts seen on any sample tested so far (see image 3.52).

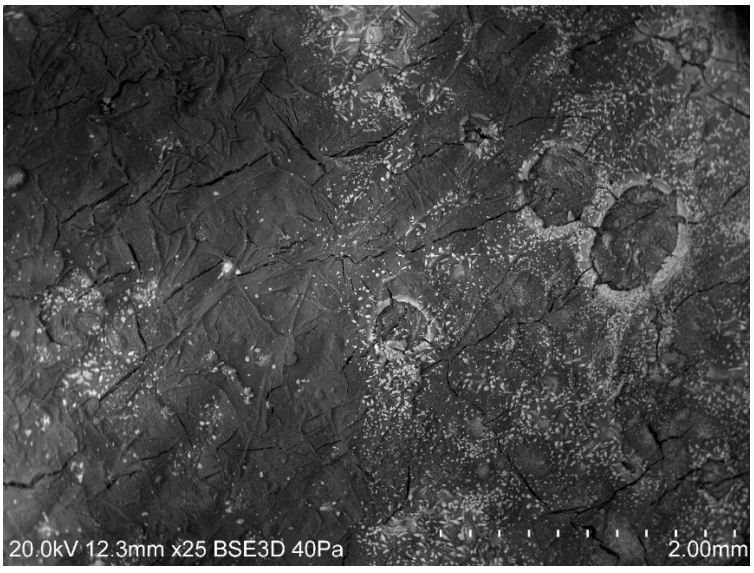


Fig. 3.51. SEM image of sample ‘U’, at the interface, treated side (left) and untreated side (right).

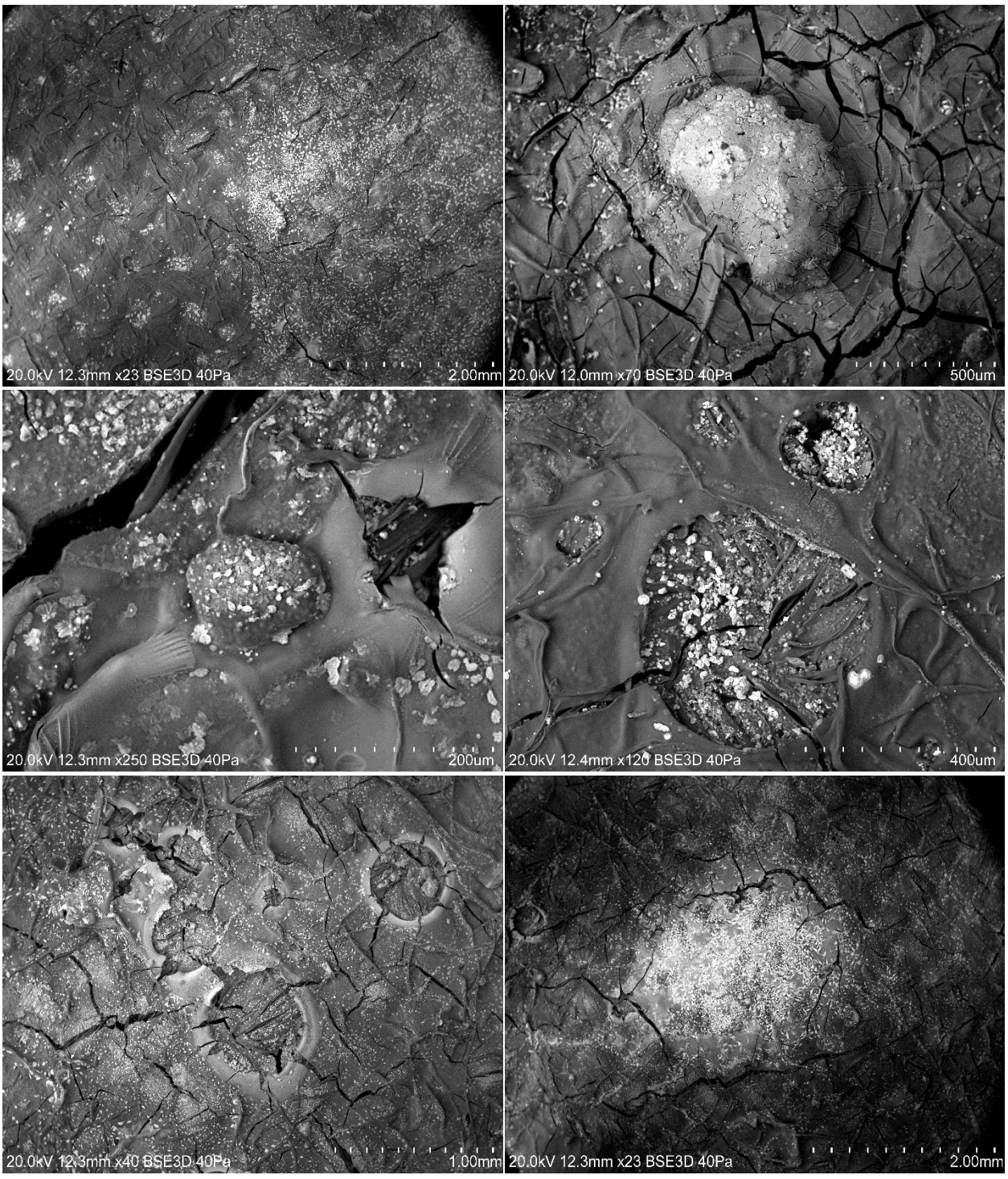


Fig. 3.52. SEM images of the completely salt ridden sample ‘U’, notice the abundance of the salts, the variety in morphology, in formations, and in their size.

Some of the salts from figure 3.52 are from the gel treated side of sample ‘U’, the treated side in general also presents a smaller but still a significant number of salts. It is unclear whether the 5% polyacrylamide acetone gel is inefficient at salt removal when compared to other gels, or whether that any other gel would have been equally inefficient at salt removal when encountered with a sample so salt-ridden as sample ‘U’.

Summary of 5min Polyacrylamide gel treatments…

The 5% polyacrylamide IPA gel applied on sample ‘R’ shows a clear increase in the efficiency of salt removal as compared to the 5% polyacrylamide butanol and acetone gels applied on samples ‘O’ and ‘U’ respectively. The butanol and acetone gels performed similarly to each other and poorer compared to the isopropanol polyacrylamide gel. None of the gels caused any surface damage on the treated mock-ups.

3.4.2.2. Gels applied for 1 hour…

Sample ‘P’ – 5% polyacrylamide butanol gel…

Performance of the 5% polyacrylamide butanol gel applied for the duration of 1h was quite similar to the efficiency seen in sample ‘O’. This particular sample mock-up had few salts to begin with and even fewer were removed by the gel (see fig. 3.53 and table 3.9).

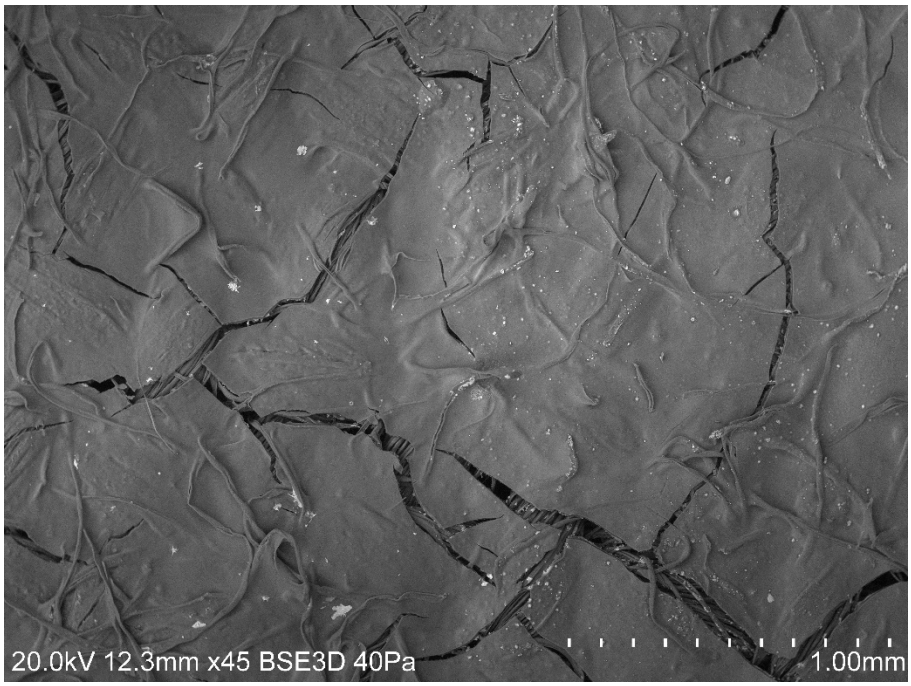


Fig. 3.53. SEM image of sample ‘P’ at the interface, treated side (left) and untreated side (right). Note that the untreated side is only barely lighter in colour than the treated side.

Table 3.9. Quantification of area scans, treated side (left) and untreated side (right).

Sample P BPA 1hr 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	21866	16.41	71.71	83.52
S	16	16534	2.43	10.64	6.18
Ca	20	9236	2.20	9.62	4.47
Mg	12	6680	1.38	6.04	4.63
P	15	3066	0.45	1.99	1.19
		Sum	**22.89**	**100.00**	**100.00**

Sample P BPA 1hr 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	25124	28.72	65.90	80.36
Ca	20	21573	5.97	13.70	6.67
S	16	27902	4.58	10.51	6.40
Mg	12	9084	2.01	4.62	3.71
K	19	6621	1.50	3.44	1.72
P	15	4815	0.80	1.83	1.15
		Sum	**43.59**	**100.00**	**100.00**

Sample ‘S’ – 5% polyacrylamide isopropanol gel…

This sample having been treated with a 5% polyacrylamide IPA gel for the duration of 1h, shows only a slight but apparent difference between the treated side and the untreated side (see fig. 3.54). The same is corroborated by the area scans of both treated and untreated sides, where there is a small decrease in the quantity of the elements Mg, S, and Ca (table 3.10). Also, it should be noted that sample ‘S’ in

general seemed to have slightly lesser number of salts (visually) as compared to some of the other analyzed samples.

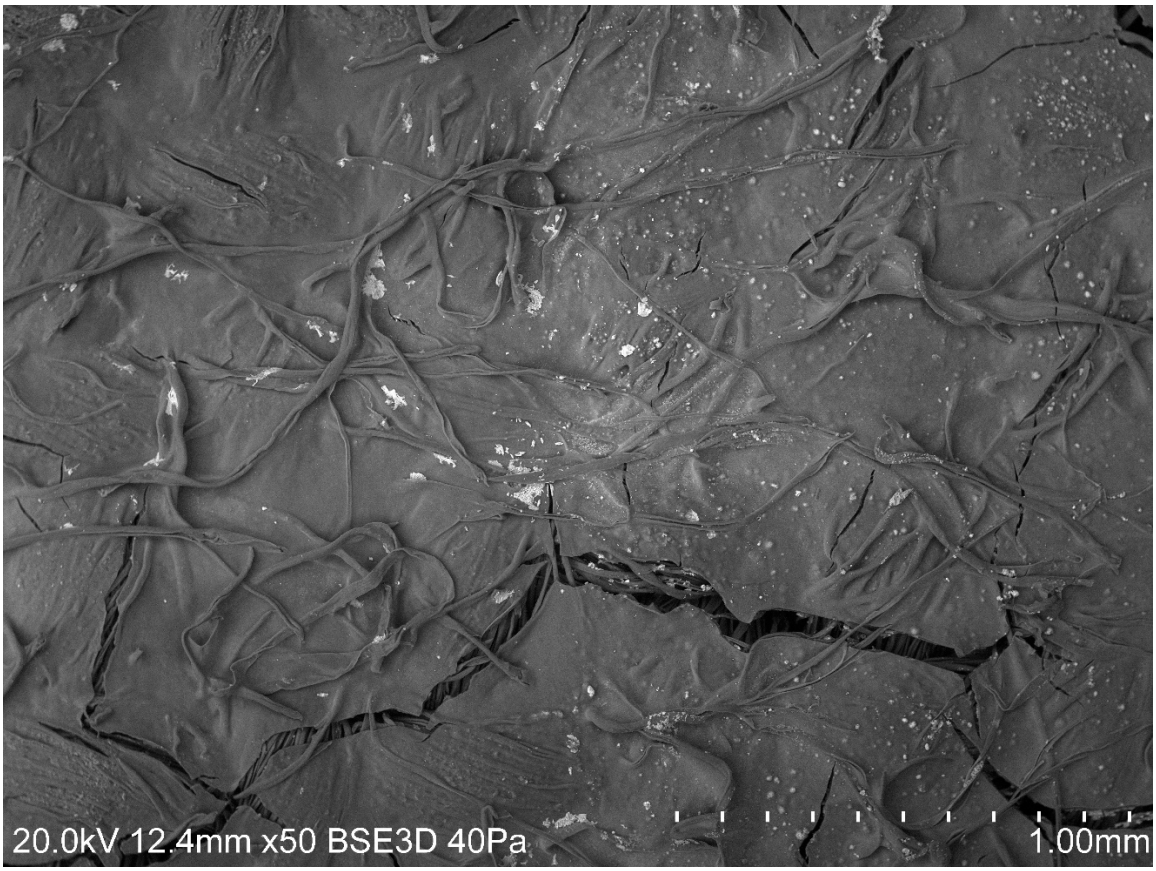


Fig. 3.54. SEM image of sample ‘S’, treated side (left) and untreated side (right).

Table 3.10. Quantification of area scans from sample ‘S’ of treated side (left) and untreated side (right).

Sample S IPAPA 1hr 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	25095	19.19	73.78	85.30
Ca	20	11967	2.72	10.47	4.83
S	16	16599	2.55	9.81	5.66
Mg	12	5393	1.04	4.00	3.04
P	15	3210	0.51	1.95	1.17
		Sum	**26.01**	**100.00**	**100.00**

Sample S IPAPA 1hr 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	24228	25.73	66.01	80.25
Ca	20	18790	4.87	12.50	6.07
S	16	25379	4.18	10.72	6.50
Mg	12	9482	1.98	5.08	4.06
K	19	6519	1.36	3.49	1.73
P	15	5125	0.86	2.21	1.39
		Sum	**38.98**	**100.00**	**100.00**

Sample ‘V’ – 5% polyacrylamide acetone gel…

Sample ‘V’ was quite abundant with salts as well, although, not as much as sample ‘U’. However, the 5% polyacrylamide acetone gel applied for a duration of 1 hour seems to have been much more efficient at salt removal (see fig. 3.55) despite the abundance of salts on the surface of sample ‘V’ (see fig. 3.56).

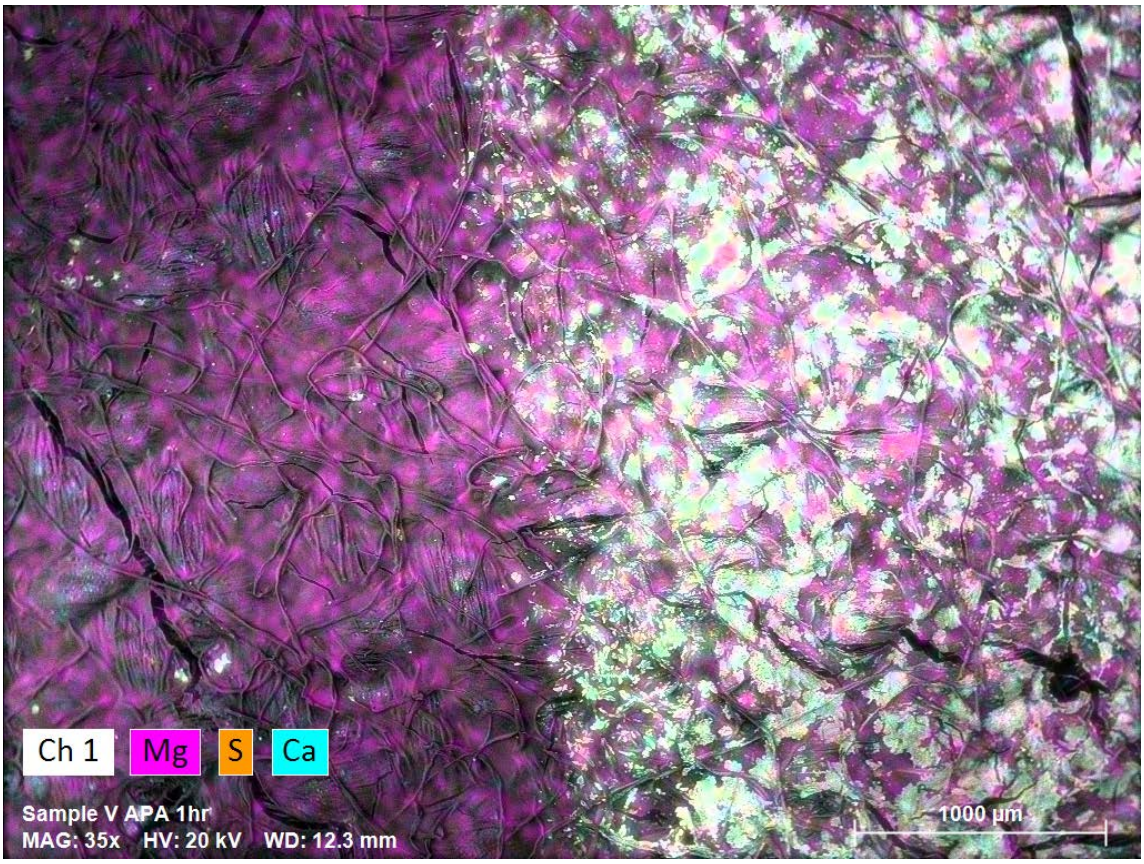


Fig. 3.55. SEM mapping image of the elements Mg, S, and Ca from the treated side (left) and the untreated side (right), note, Mg is present on both sides as it is part of the dolomitic layer.

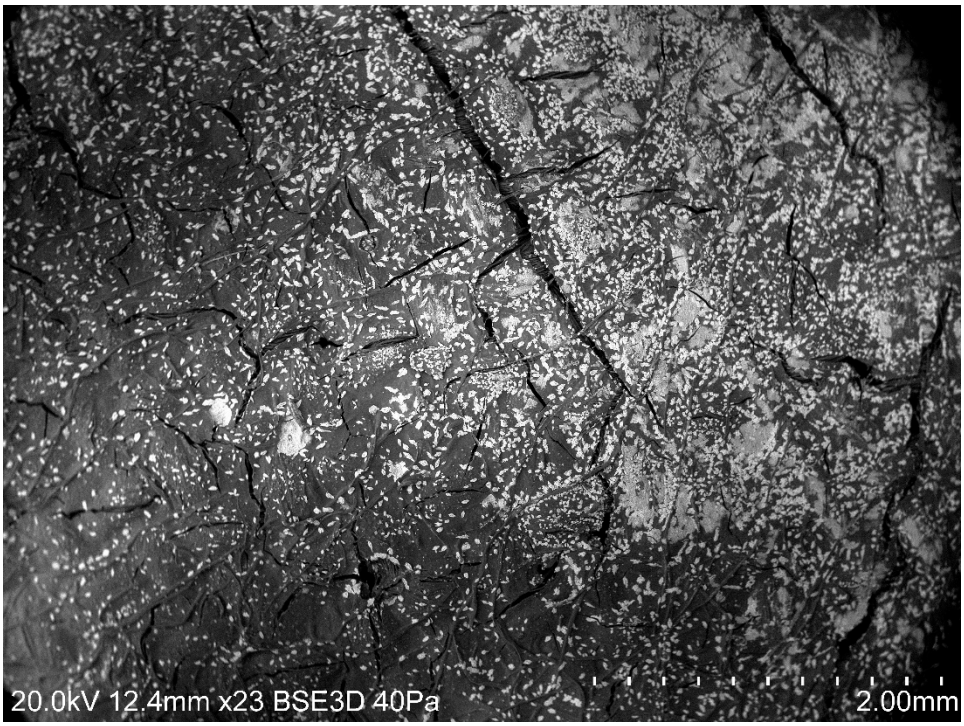


Fig. 3.56. SEM image of a large area of the untreated surface of sample ‘V’ almost completely saturated with salts.

Also of note was the lack of any structural surface damage caused by the gel.

Summary of 1h polyacrylamide gel treatments…

The 5% polyacrylamide acetone gel applied on sample ‘V’ performed with excellent efficiency in salt-removal, the isopropanol gel also had very good efficiency in salt-removal, whereas the 5% polyacrylamide butanol gel comparatively was the worst performer. However, none of the gels caused any surface damage to the treated mock-ups.

3.4.2.3. Gels Applied for 3 days…

Sample 'Q' – 5% polyacrylamide butanol gel…

Looking at the interface region of sample 'Q' where the treated side meets the untreated side, two things seem clear; there are not inherently too many salts on the untreated surface, and that the 5% polyacrylamide butanol gel applied for 3 days seems to be quite efficient in salt removal (see fig. 3.57).

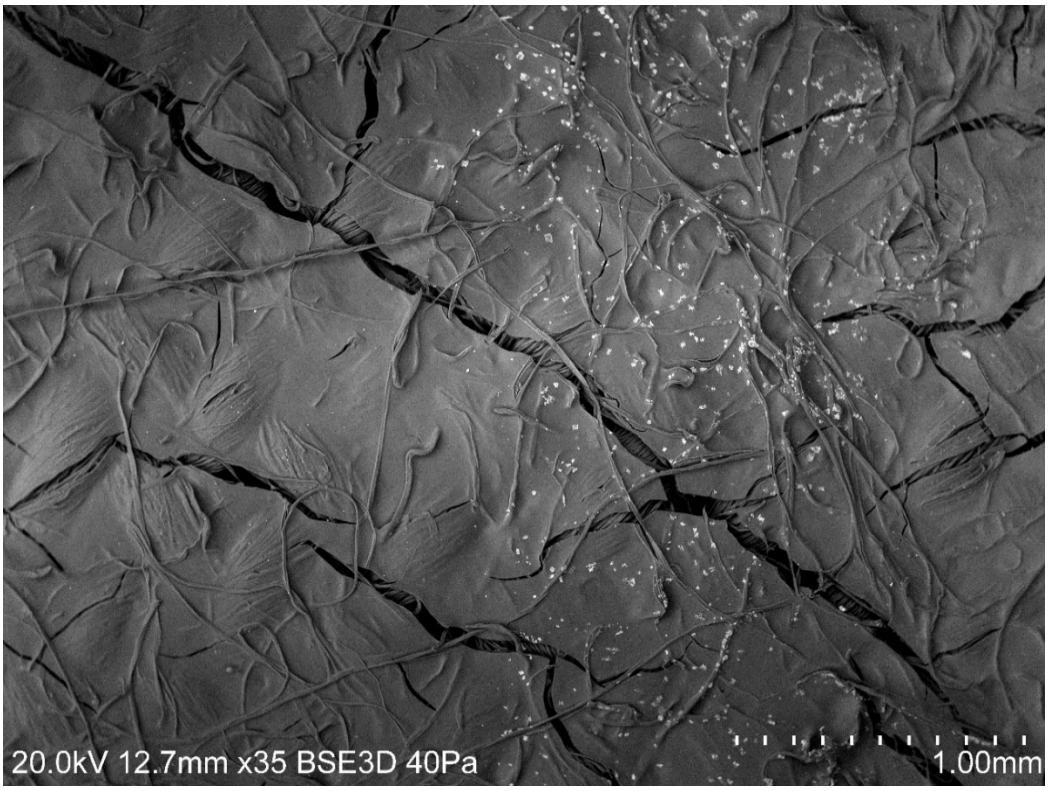


Fig. 3.57. SEM image of sample 'Q' at the interface, treated side (left) and untreated side (right). Note how salt-free the treated side appears, and also note the presence of only a few salts on the untreated side.

The gel treated side of sample 'Q' appeared exceptionally salt-free, more so than other treated and tested samples, and an area scan of the treated side revealed the lack of even trace amounts of elemental Mg, only minute amounts of Ca, but a decent amount of sulfur (see fig. 3.58 & table 3.11)

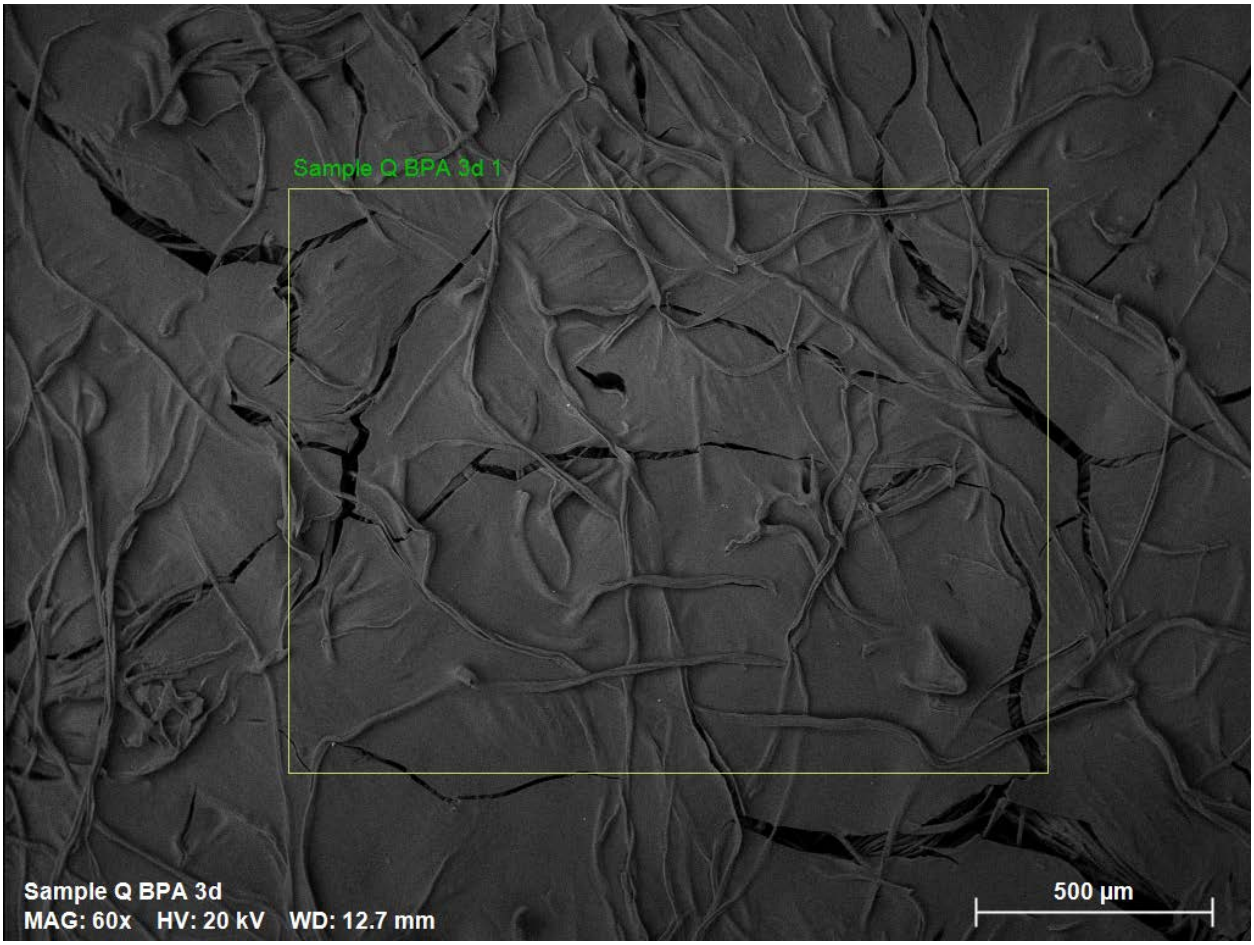


Fig. 3.58. Area scan image of the treated side of sample ‘Q’, note the complete lack of presence of any crystalline formation of salts.

Table 3.11. Quantification of area scan of the treated side of sample ‘Q’.

Sample Q BPA 3d 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	25203	12.99	78.29	87.91
S	16	25019	3.23	19.46	10.90
P	15	1721	0.22	1.34	0.78
Ca	20	706	0.15	0.90	0.41
		Sum	**16.59**	**100.00**	**100.00**

Note the complete lack of elemental Mg, and the presence of only a minute amount of Ca.

XRD…

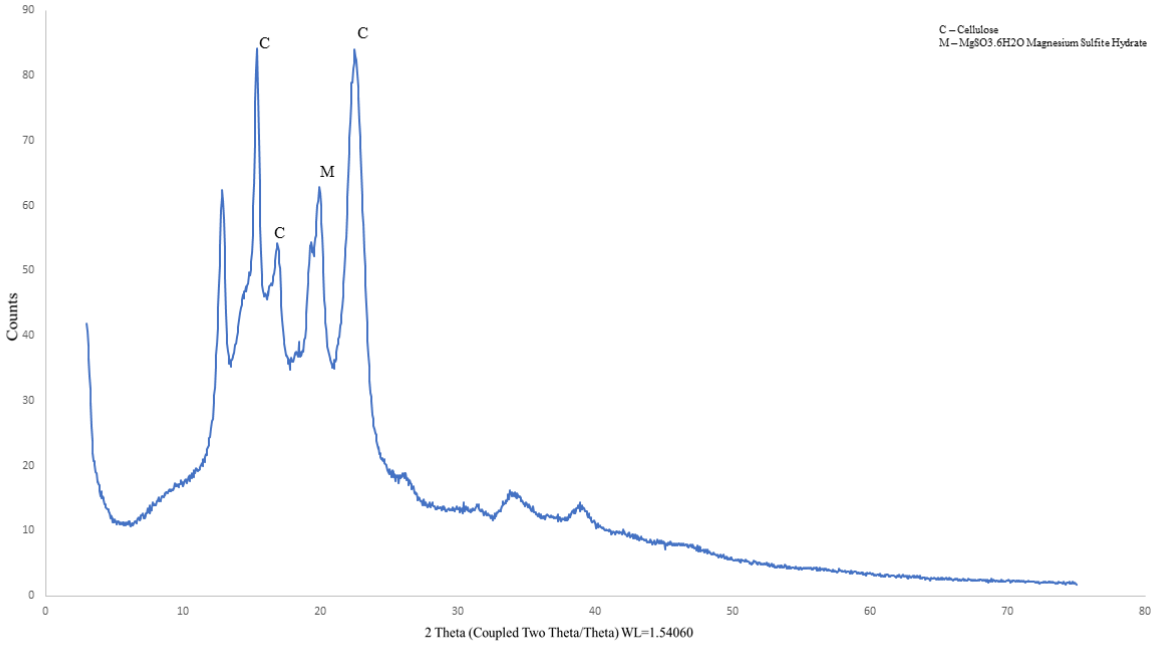


Fig. 3.59. Diffractogram of treated side of sample ‘Q’, showing peaks of Cellulose and magnesium sulfite hydrate ($MgSO_3.6H_2O$).

In the figure above the usual cellulose peaks are present while the calcite peak at 2theta value of 30 is absent. Also note the magnesium sulfite hydrate peak at 2theta value of 20 whose peak intensity is higher (60 as compared to around 40 counts usually) than many of the other analyzed gels.

Sample ‘T’ – 5% polyacrylamide isopropanol gel…

Sample ‘T’ was treated for 3 days with a 5% polyacrylamide IPA gel. This treatment seems to be incredibly effective in the removal of salts and in general the lessening of elements Mg, Ca and S. The difference between the treated and untreated side of sample ‘T’ is quite evident and in general the area scans of the treated side reveal the lowest values of the elements Mg, Ca and S, seen from any sample so far tested and analyzed (see fig. 3.60, fig. 3.61 & table 3.12).

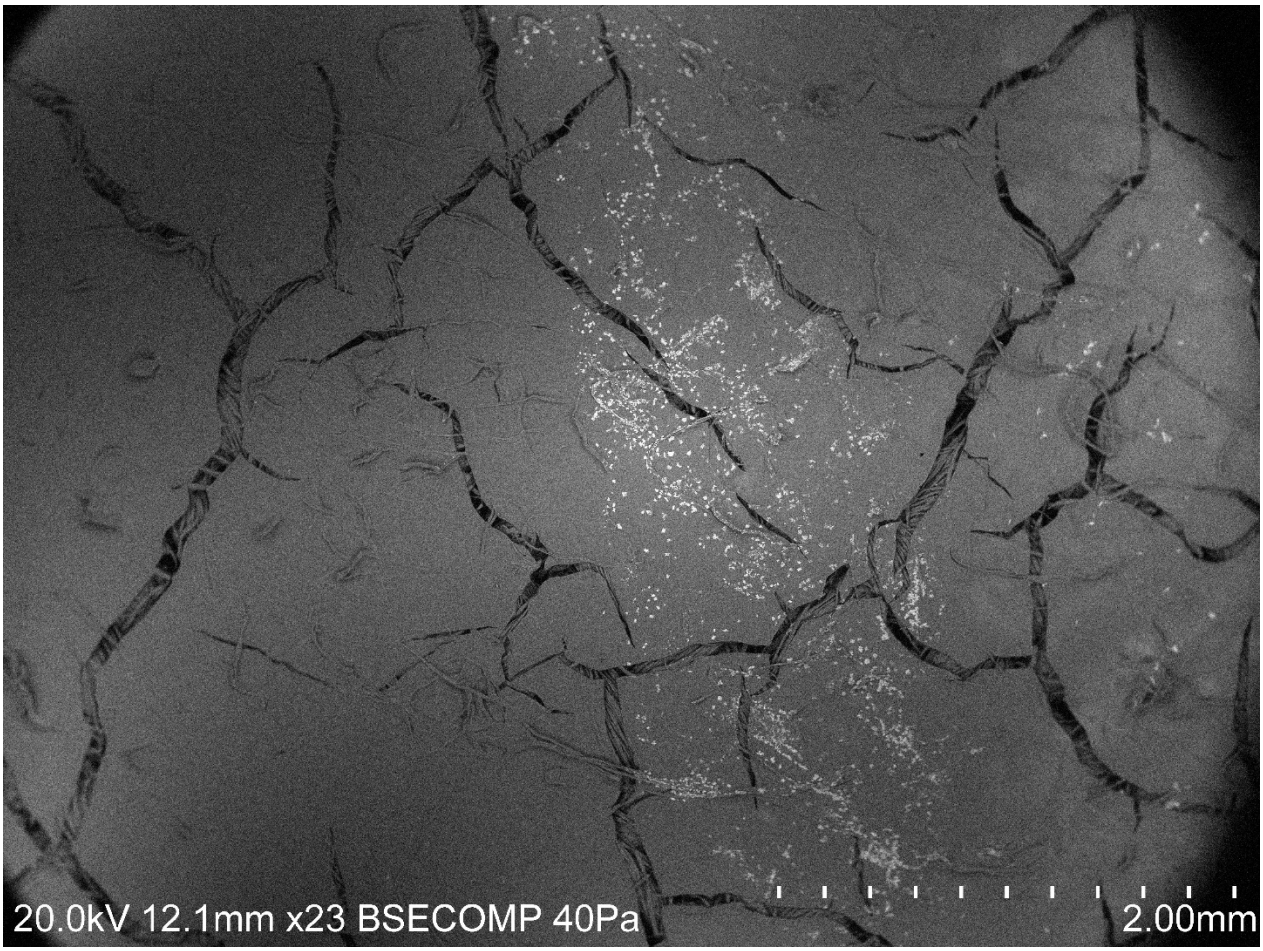


Fig. 3.60. SEM image of sample ‘T’ showing a very clear difference between the interface where the treated side (left) meets the untreated side (right).

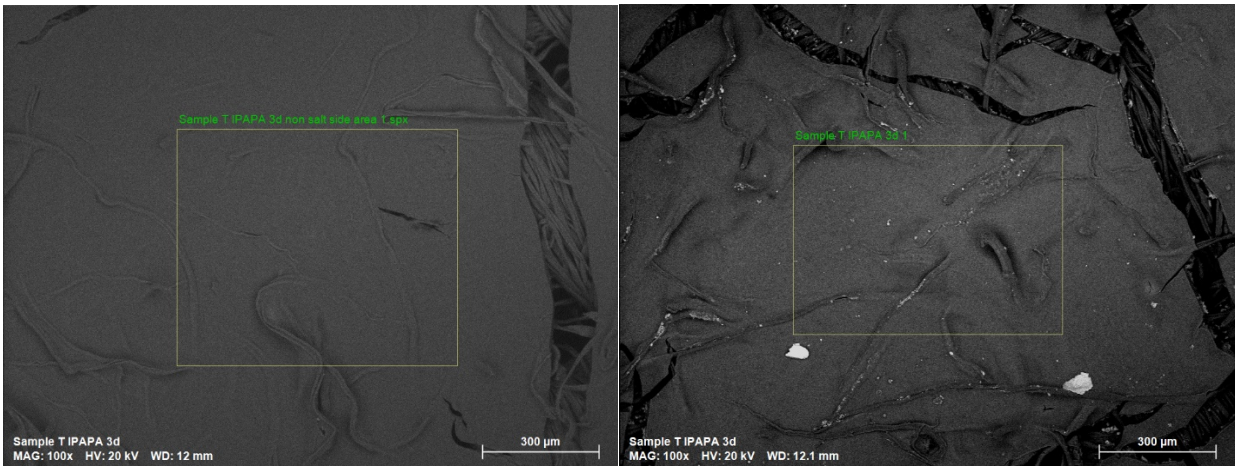


Fig. 3.61. SEM images of area scans of the treated side (left) and the untreated side (right).

Table 3.12. Quantification of area scans from sample ‘T’ of treated side (left) and the untreated side (right).

Sample T IPAPA 3d 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
P	15	2227	0.21	0.21	0.09
S	16	26472	2.49	2.49	1.03
Na	11	138	0.02	0.02	0.01
Mg	12	43	0.01	0.01	0.00
K	19	213	0.03	0.03	0.01
Ca	20	327	0.05	0.05	0.02
C	6	72103	66.05	66.05	73.00
O	8	26986	31.15	31.15	25.84
		Sum	**100.00**	**100.00**	**100.00**

Sample T IPAPA 3d 1

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]
O	8	25039	29.79	62.35	77.48
S	16	41135	6.79	14.21	8.81
Ca	20	23727	6.67	13.96	6.92
Mg	12	12416	2.76	5.78	4.72
K	19	4960	1.15	2.41	1.23
P	15	3701	0.62	1.30	0.84
		Sum	**47.78**	**100.00**	**100.00**

Note how in the above table, only a trace amount of the element Mg remains on the gel treated side, and the elements Ca and S are also found in very minute quantities. A few more area scans were executed which showed very similar results. And most importantly unlike in some other sample mock-ups that were treated for 3 days with a gel (loaded/unloaded, agarose/polyacrylamide) no instance of any mold/fungi growth was noted nor was any type or form of structural damage seen on the sample surface. This, coupled with the incredible efficiency in the removal of salts lends this particular 5% polyacrylamide IPA gel with a treatment duration of 3 days to be the best performing gel tested so far.

XRD…

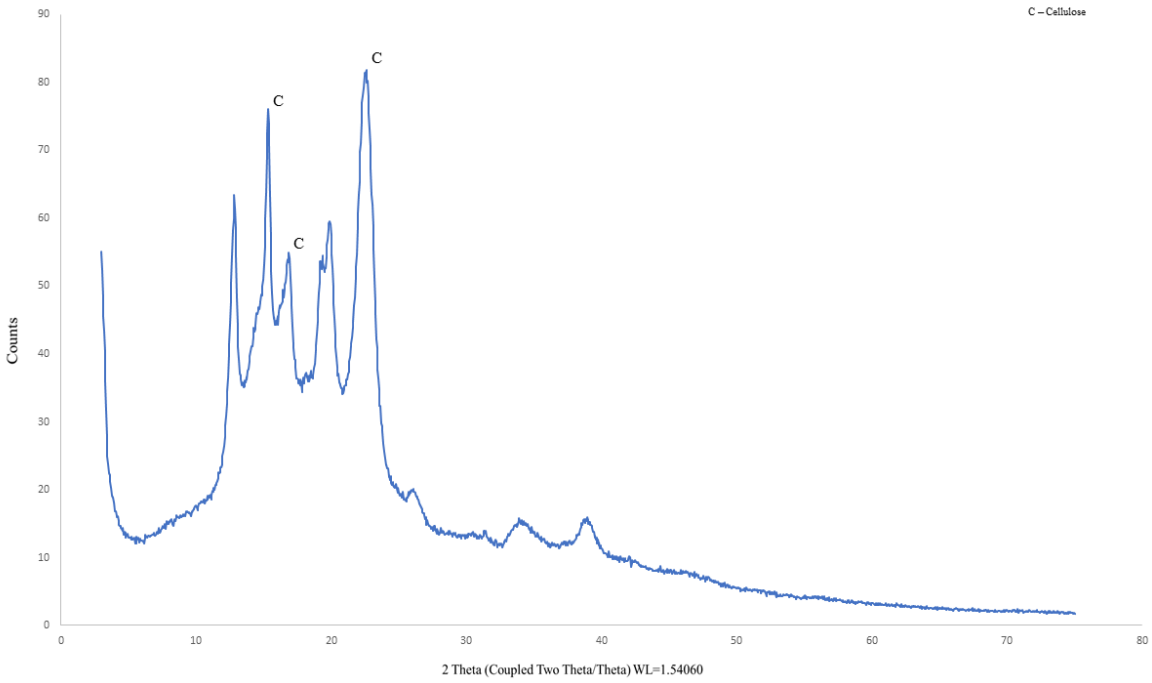


Fig. 3.62. Diffractogram of sample ‘T’ showing cellulose peaks.

Note in the fig. 3.62 the lack of a calcite peak which is generally present near the 2theta value of 30 in diffractograms of some other samples. This lack of a calcite peak indicates a good reduction in the salts present on the sample surface which would also be in line with the data acquired from SEM-EDS.

Sample ‘W’ – 5% Polyacrylamide Acetone Gel…

The 3-day long treatment of sample ‘W’ with a 5% polyacrylamide acetone loaded gel seems quite successful in the removal of salts. The region of the interface of treated and untreated side shows this quite well (see fig. 3.63). In fact, the gel seems to be very efficient at salt removal, as much of the area of the treated side are for the most part completely salt-free (see fig. 3.64). Surprisingly, the surface condition of the treated side seems to be undamaged even after a 3-day exposure to

a gel loaded with acetone, and no growth of mold / fungi is noted on the treated side too.

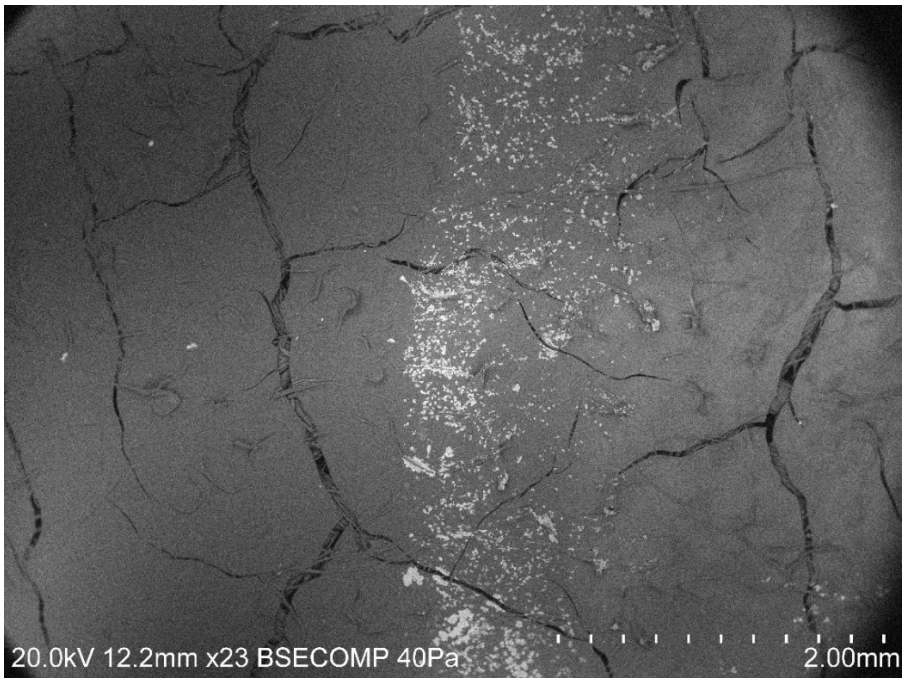


Fig. 3.63. SEM image of sample ‘W’, treated side (left) and untreated side (right).

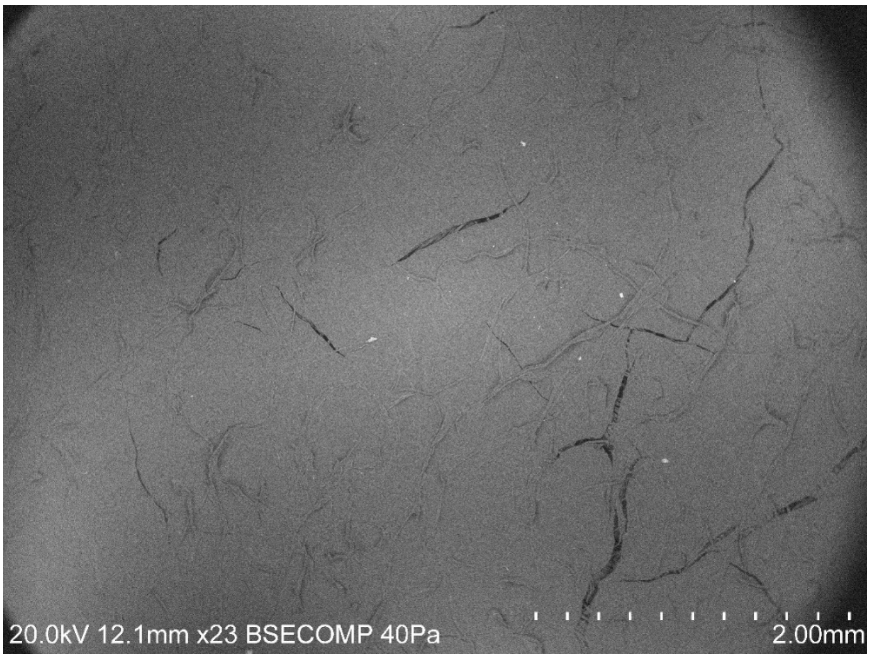


Fig. 3.64. SEM image of the gel treated area of sample ‘W’, note that it is nearly salt-free and damage-free.

However, on this instance the untreated side of sample ‘W’ presents with multiple separate growths of mold / fungi, and severe damage to the surface structure coupled with an extreme saturation of salts (see fig. 3.65).

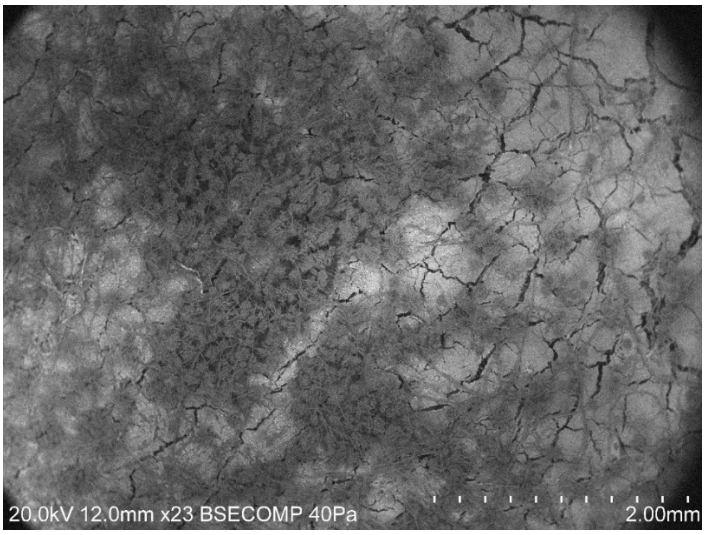


Fig. 3.65. SEM image of mold coverage, surface damage and salt saturation of sample ‘W’.

Note that in the above image, the entire visible surface that isn’t the mold/fungi is actually salts and hence the extremely light grey / white colour of the surface. And although most of the fungal growth is on the untreated side, it was most likely caused by the water and cleaning solution run-off from the 5% polyacrylamide acetone gel that must have slowly leached into the untreated side which in turn also caused the surface damage.

XRD…

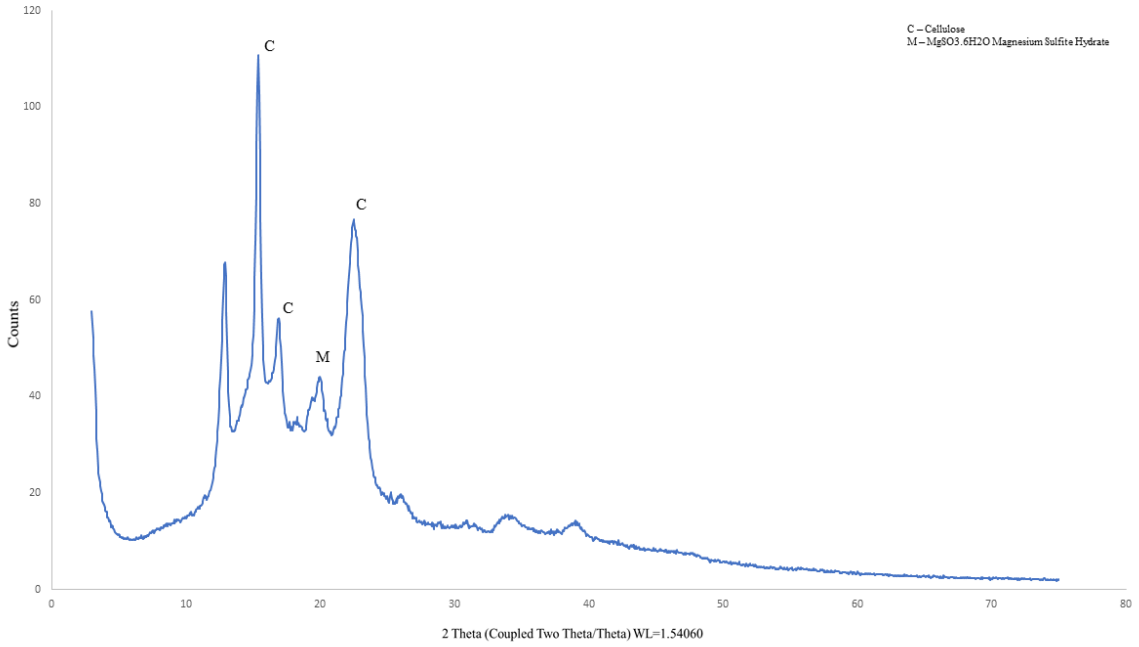


Fig. 3.66. Diffractogram of sample ‘W’ showing peaks of cellulose and magnesium sulfite hydrate ($MgSO_3.6H_3O$).

In the fig. 3.66, note once again a lack of peak at 2theta value of around 30, indicating the lack of presence of calcite on the treated side and also note the peak of magnesium sulfite hydrate which is weaker when compared to other diffractograms of gels lesser in salt-removal efficiency.

Summary of 3-day polyacrylamide gel treatments…

The 5% polyacrylamide butanol gel applied on sample ‘Q’ shows excellent efficiency in salt-removal, while both the 5% polyacrylamide isopropanol and acetone gels applied on samples ‘T’ and ‘W’ perform exceptionally well at removing salts. However, while samples ‘Q’ and ‘T’ showed no signs of surface damage at all, sample ‘W’ treated with the acetone gel, showed on the untreated side (surprisingly) extreme surface deterioration.

3.5. Comparative Analysis…

With all of the analytical data obtained from the SEM-EDS and XRD analysis of all agarose and polyacrylamide gel treated mock-ups, a qualitative and comparative table has been made that highlights mainly the 'cleaning or salt-removal efficiency' and the 'structure / surface damaging' aspects of all applied gels at all time steps.

For the purposes of the table, the descriptive names of both the agarose and polyacrylamide gels have been abbreviated as follows:

Table 3.13. Abbreviations of all formulated agarose and polyacrylamide gels.

Unloaded Agarose gel = ULA	Unloaded Polyacrylamide gel = ULPA
Butanol Agarose gel = BA	Butanol Polyacrylamide gel = BPA
Isopropanol Agarose gel = IPAA	Isopropanol Polyacrylamide gel = IPAPA
Acetone Agarose gel = AA	Acetone Polyacrylamide gel = APA

A unique gel rating system was created in order to better realize both the 'cleaning or salt-removal' and 'structural / surface damaging' properties of all tested gels:

*Table Legend:

In Cleaning Efficiency

+	Good / relatively poor
++	Very good/well
+++	Excellent
++++	Exceptional
---	Very bad/poor

In Structural / Surface damage

---	No damage at all
+	Some damage
+++	Extreme damage

The structure of the table follows the same structure adopted in the presentation of the results so far.

Table. 3.14. Qualitative analysis of all agarose and polyacrylamide gel treated samples.

Treatment Duration	Sample Name	Type of gel	Cleaning Efficiency	Structural/surface Damage
2 hours	'1/2'	4% ULA gel	+	---
	'1'		+	---
5 mins	'M'	5% ULPA gel	++	---
1 hour	'N'		+	---
5 minutes	'C'	3% BA gel	++	---
	'F'	3% IPAA gel	+	---
	'I'	2% AA gel	+	---
	'O'	5% BPA gel	+	---
	'R'	5% IPAPA gel	++	---
	'U'	5% APA gel	+	---
1 hour	'D'	3% BA gel	++	---
	'G'	3% IPAA gel	++	---
	'J'	2% AA gel	++	---
	'P'	5% BPA gel	+	---
	'S'	5% IPAPA gel	++	---
	'V'	5% APA gel	+++	---
3 days	'E'	3% BA gel	++	+
	'H'	3% IPAA gel	+++	+++
	'K'	2% AA gel	---	+++
	'Q'	5% BPA gel	+++	---
	'T'	5% IPAPA gel	++++	---
	'W'	5% APA gel	++++	+++

From the above table and its rating system several factors regarding the ‘cleaning or salt-removal’ and the ‘structural / surface damaging’ capabilities of the gels become very apparent:

On the Cleaning Efficiency of the Gels by Treatment Duration…

The longer the duration of the treatment, the greater the salt-removal capability of the gel. For instance, among all 6 of the various loaded gels (agarose and polyacrylamide) that were applied on various samples for the duration of 5 minutes, only 2 gels have scored a ‘very good’ (++) rating in the category of cleaning efficiency. The rest of the 4 gels only managing to score a ‘good’ or ‘relatively poor’ (+) in the same category.

This point is furthered when considering the ‘cleaning efficiency’ of all 6 of the gels (agarose and polyacrylamide) that were applied for a duration of 1 hour. In this category 4/6 gels score a ‘very good’ (++) rating, 1 gel scores an ‘excellent’ rating (+++) and one more scored a ‘good’ or ‘relatively poor’ (+) rating.

Lastly, in the 3-day treatment duration group of gels (agarose and polyacrylamide), the only two ‘exceptionally’ (++++) performing gels among all of the tested gels are present, while also having two ‘excellently’ (+++) performing gels, one ‘very good’ (++) gel and lastly one ‘very poorly’ (---) performing gel.

On the Damaging Capability of the Gels by Treatment Duration…

However, when considering the ‘structural / surface damaging’ capabilities of the gel, another factor is also made quite apparent;

The longer the duration of gel treatment, the greater the risk of surface damage in the form of discoloration, mold/fungi or total surface deterioration.

None of the gels (agarose or polyacrylamide, loaded or unloaded) tested for the durations of 5min, 1 hour, or 2 hour have caused any noticeable structural or surface damage at all. Whereas, 4/6 gels tested for the duration of 3 days have caused very noticeable surface damage to the sample mock-ups. One such gel caused 'some damage' (+) to the treated mock-up in the form of discoloration, and 3 other gels caused 'extreme damage' (+++) to the treated surface in the form of heavy growth of mold / fungi or outright deterioration of the canvas surface.

On the Most Effective Gel and Cleaning Solution…

Quite clearly the 5% polyacrylamide gel loaded with isopropanol outperforms all other gels in the 'cleaning efficiency' category. The gel scored a 'very good' (++) twice and an 'exceptional' (++++) for the treatment durations of 5min, 1h, and 3 days respectively.

On the Most Damaging Gel and Cleaning Solution…

Although no singular type of gel i.e., agarose or polyacrylamide gel was noticed to be the most damaging to the treated surface, gels loaded with acetone were regularly causing more damage to the treated surface. Both of the extremely damaged mock-ups were treated with a gel loaded with acetone and also treated for a duration of 3 days.

On Agarose Gels…

The unloaded / plain 4% agarose gels which were applied for 2 hours perform poorly at removal of salts but they did not cause any structural damage to the sample mock-up.

The 3% agarose butanol gels applied for all time steps are very good at salt removal, but only the gel applied for 3 days (on sample 'E') caused additional

yellowing of the mock-up and the development of a foul odor, suggesting the natal stages of mold / fungi growth.

The cleaning efficiency of the 3% agarose isopropanol gel seems very time dependent as the gels applied for 5min, 1 hour, and 3 days performed poorly, very well and excellently, respectively. Once again, the gel applied for 3 days (on sample 'H') was damaging to the mock-up as a growth of mold / fungi was observed.

The 2% agarose acetone gel was unremarkable for its cleaning capabilities in the 5min step, performing poorly., but performing very well in the 1-hour category. But it was most remarkable for being extremely destructive toward the treated sample ('K') mock-up, as not only the gel treated side presented with significantly more salts than the untreated side, the dolomitic casein layer was completely eroded/ deteriorated along with significant damage to the underlying cotton canvas.

On polyacrylamide Gels…

The unloaded / plain 5% polyacrylamide gel applied for 5min performed very well without any structural damage to the mock-up while the same gel applied for 1 hour performed relatively poorly, also without any structural damage. This is very conflicting data and further experimentation is necessary to form any absolute conclusions.

The 5% polyacrylamide butanol gels applied for 5min and 1 hour were 'good' at salt removal, while the same gel applied for 3 days was excellent at salt removal. None of the gels caused any noticeable structural damage to the mock-ups.

The 5% polyacrylamide isopropanol gels performed very well at time steps of 5min and 1 hour, while performing exceptionally at 3 days on sample ‘T’. None of the treated samples showed any signs of surface damage.

The cleaning efficiency of the 5% polyacrylamide acetone gels were very varied at each time step. The gels performed poorly, excellently, and exceptionally at 5min, 1 hour and 3 days respectively. But surprisingly the acetone gel treated side of sample ‘W’ (treated for 3 days) showed almost no salts and certainly no surface damage at all. While, the untreated side of sample ‘W’ was not only full of salts, and mold/fungi, but the surface was also fully eroded and deteriorated, very similarly to that of sample ‘K’.

Agarose Vs Polyacrylamide gels…

When considering factors such as, ease of gel preparation the agarose gel is far simpler to prepare as it involves only two ingredients (agarose and water) and applied heat, while the polyacrylamide gel involves many more ingredients in very specific ratios and quantities. However, considering gel strength/workability, the polyacrylamide gel is very resilient against breakage whilst being very flexible unlike the agarose gels that were in general more fragile (user error could be a factor).

Regarding the cleaning efficiency of both gels; in table (3.14) the polyacrylamide gel scored a total of 24+, including two exceptionally performing gels (on sample ‘W’ & ‘T’) and two excellently performing gels (sample ‘V’ & ‘Q’). whereas the agarose gels only managed a score of 17+, with only one excellently performing gel (sample ‘H’) and no exceptional gels at all.

Regarding structural / surface damage, only one polyacrylamide gel treated sample (‘W’) showed extreme compromise in structural integrity, whereas two

samples (‘K’ & ‘H’) treated with an agarose gel showed extreme surface damage along with another sample (‘E’) that presented with discoloration and a foul odor.

CHAPTER 4

CONCLUSIONS

Edvard Munch’s Aula Magna preparatory sketches were stored in less-than-ideal conditions and this caused the development of salt efflorescence on their surface, which is extremely detrimental to their preservation. Hence, there was the utmost need for its treatment and conservation.

The main goal of the present thesis was to find a cleaning solution that was effective in either the removal or stabilization of salts, specifically calcium and magnesium sulfates.

And to this purpose mock-ups imitating the structure and composition of the sketches were created and artificially aged so that the process of salt formation could be accelerated.

And once the salts were formed, the removal or stabilization of them was to be achieved through formulations of cleaning solution loaded agarose and polyacrylamide gels. The gels act as excellent delivery vehicles for any cleaning solution that would be loaded onto them. The cleaning solutions were chosen to be alcohols; butanol, isopropanol and acetone as they are readily available and commonly used as cleaning agents.

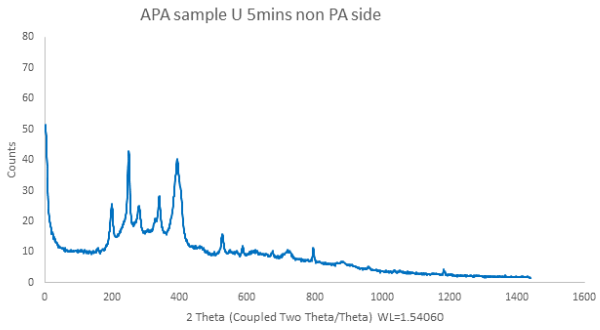
Thus, eight unique formulations of agarose and polyacrylamide gels both unloaded and loaded with alcohols were created and subsequently tested on the sample mock-ups at multiple time steps in order to determine which gel was most efficient at salt removal.

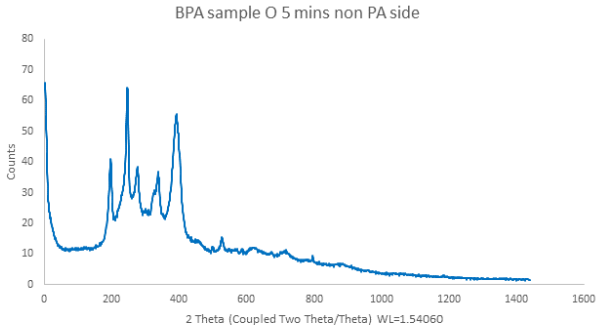
SEM-EDS and XRD analysis of all the gel treated sample mock-ups revealed that the 5% polyacrylamide isopropanol gel performed with the best salt-removal efficiency overall. The gel specifically did very well at time steps of 5 minutes and 1 hour, while performing exceptionally well after 3 days of application on the sample mock-up. None of the 5% polyacrylamide isopropanol gel showed any signs of surface damage after application. This cleaning efficiency coupled with the general ease of workability of polyacrylamide gels over agarose gels, makes this formulation of gel and cleaning solution the most desirable among the other tested gels.

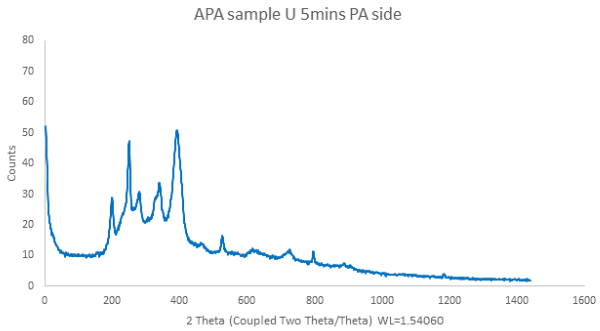
This technique of salt removal via agarose and polyacrylamide gels can be furthered by perhaps utilizing a broader range of cleaning solutions whether alcohols or otherwise to be loaded into the gel. The percentage of the formulated gels and the percentage of the loaded cleaning solutions can also be manipulated in order to affect changes in the outcome of the treatment. Finally, many more and diverse time steps can be added towards the treatment duration to find not only the most efficient duration for salt-removal but also to weed out treatment durations that are detrimental to the treated surface itself.

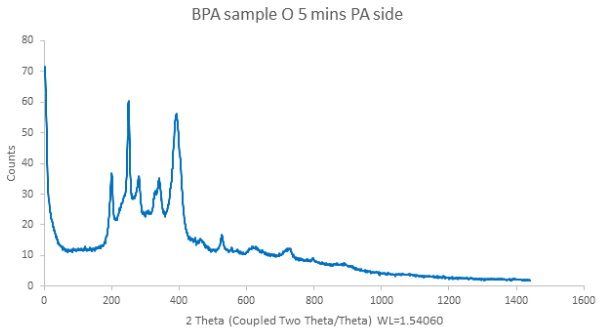
APPENDIX I

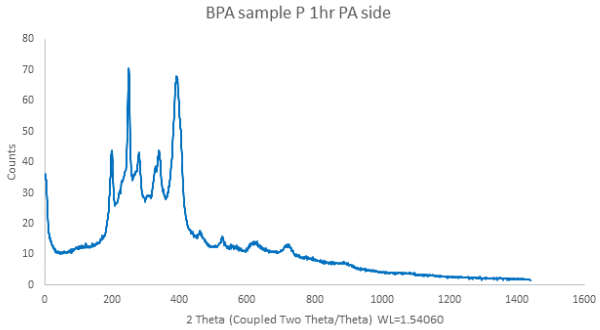
Diffractograms of samples; U, O, P, R, V, S K, C, J, M, N, I, F, D, G.

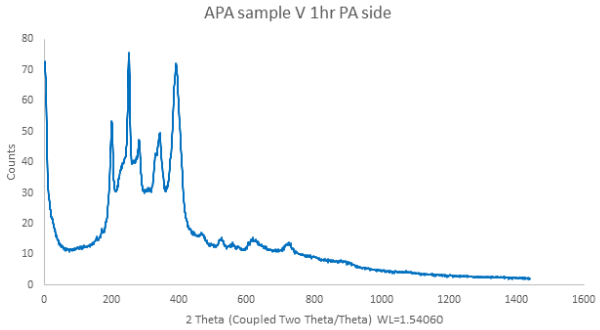


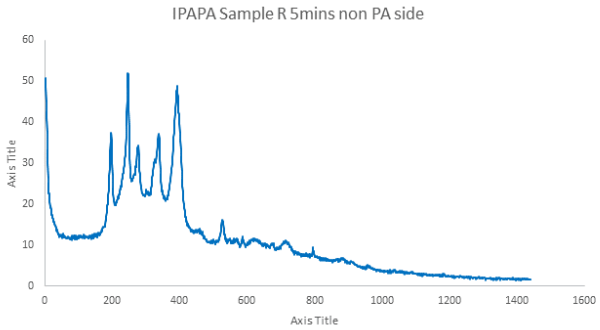


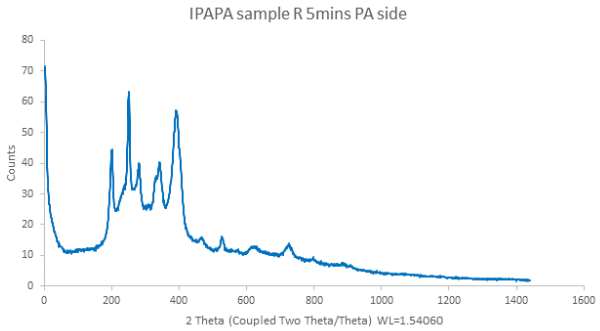


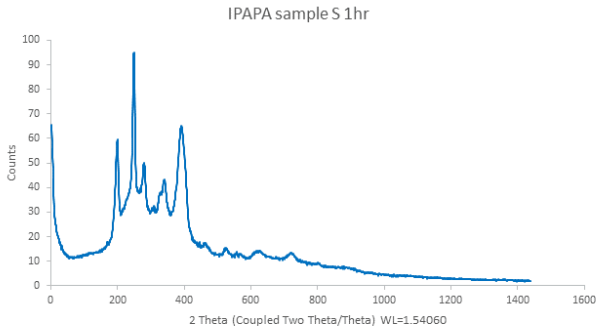








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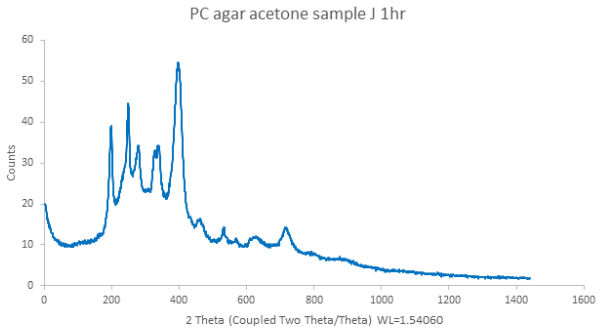
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Counts
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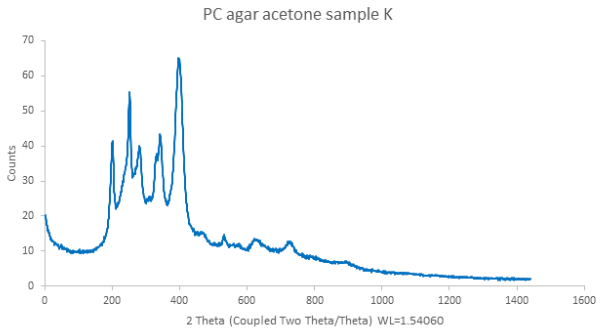
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Counts
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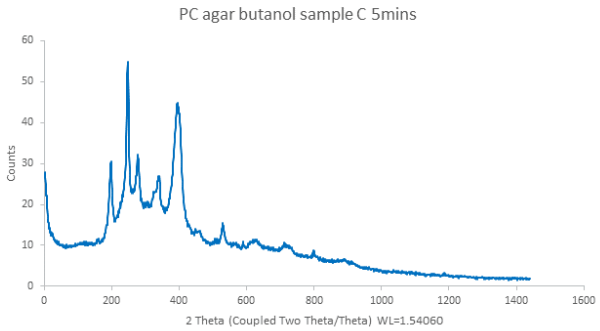
PC agar butanol sample C 5mins
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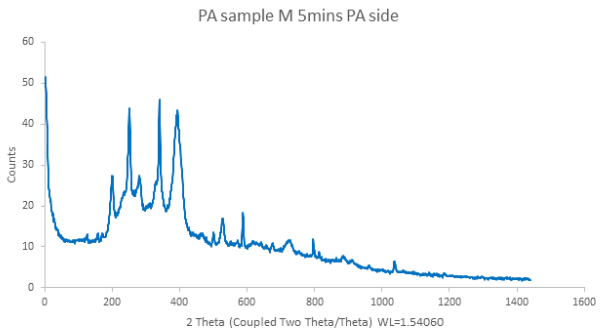
PA sample M 5mins PA side
Counts
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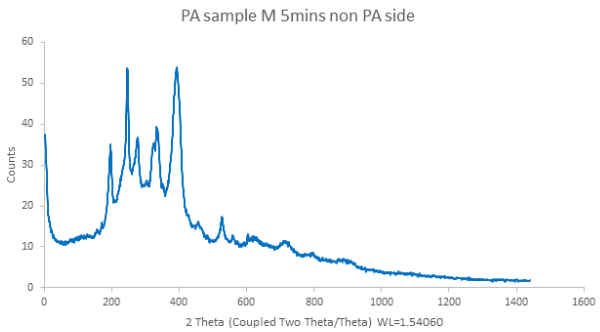
PA sample M 5mins non PA side
Counts
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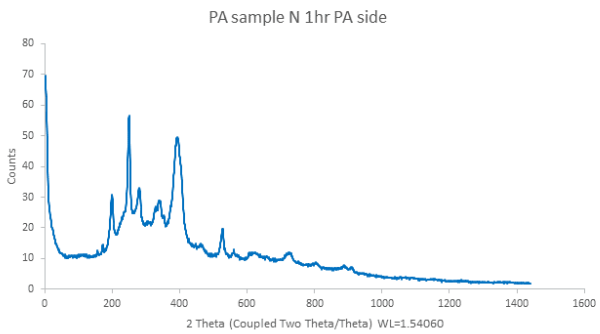
PA sample N 1hr PA side
Counts
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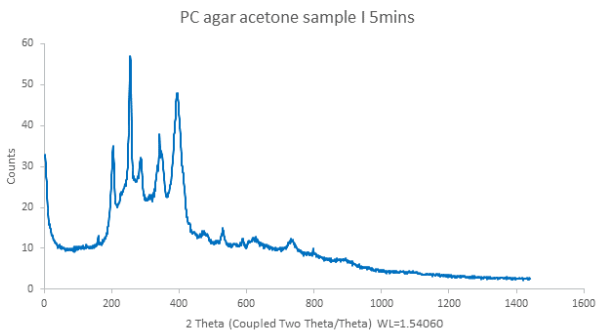
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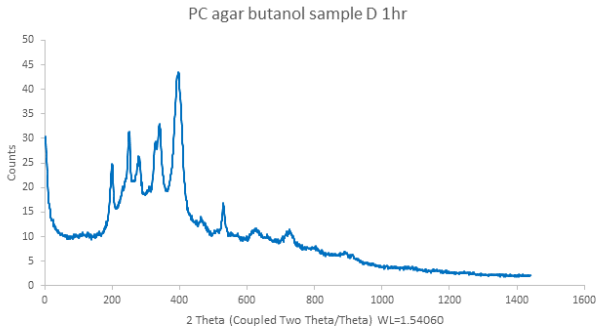
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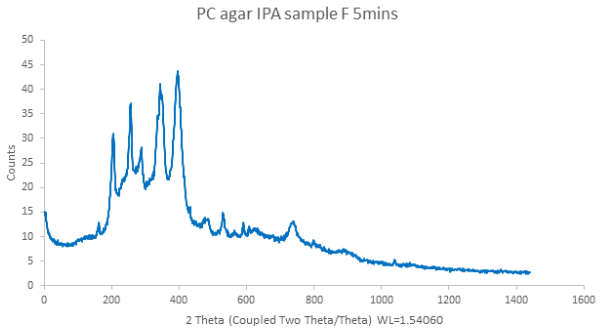
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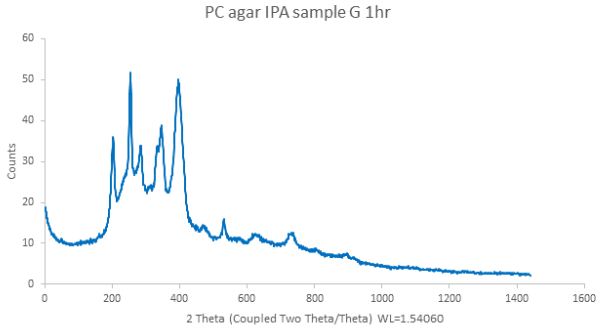
PC agar IPA sample G 1hr
Counts
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