

DEVELOPMENT OF A NOVEL METHOD TO REDUCE THE IMPACT OF CUTANEOUS CHEMICAL ATTACKS

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Abstract. Chemical attacks are a global problem: from 2011 to 2016 there were 1,464 incidents involving a corrosive substance in London alone. The most common chemicals used in these attacks are sulfuric, nitric and hydrochloric acids. Concentrated solutions of strongly alkaline substances including sodium hydroxide and sodium hypochlorite are also used. Current first-aid advice suggests diluting the exposed area with water and transfer to a hospital for further treatment. An immediate neutralisation treatment is avoided as incorrect identification of the corrosive could worsen the damage. In addition, there are concerns the enthalpy of solvation and neutralisation causes secondary burns. These limitations demonstrate the need for an amphoteric neutralising treatment with a low enthalpy of neutralisation. Aqueous formulations of natural water-based surfactants with natural plant-based substances have been trialled as neutralisers of sulfuric acid, sodium hydroxide and sodium hypochlorite. pH titrations demonstrated that the natural formulations are amphoteric, capable of effectively neutralising acidic and alkaline corrosives with minimal heat of neutralisation and no gas evolution. In addition, the studies have shown that the formulations can reduce oxidising compounds such as sodium hypochlorite. The experiments compared intact collagen with attacked but untreated collagen and collagen that had a corrosive applied but followed by treatment at different time intervals. Scanning electron microscopy (SEM) showed the reaction with concentrated sulfuric acid is rapid; significant collapse and gelatinisation of the fibre structure was observed within 5 seconds. Pigskin was utilised to model human skin: the observations demonstrated the importance of the epidermis in protecting the skin from chemical damage. Five minutes exposure to sulfuric acid, sodium hydroxide and sodium hypochlorite did not penetrate the epidermis, although damage was observed. The formulations of natural products recently tested at the University of Northampton have been shown to mitigate secondary chemical burns, whereas treatment with water alone resulted in secondary burns due to residual corrosive in the skin structure not being neutralised. The trials indicate that the product could be usefully applied by first responders and emergency services personnel.

1 Introduction

Chemical attack is defined as the act of throwing a corrosive substance onto the body of another with intent to harm the eyes, skin and deeper body tissues.ⁱ The possible long-term physical consequences of these attacks include blindness, scarring of the skin tissue.ⁱⁱ The most common types of acid used in these attacks are sulfuric and nitric acid.ⁱⁱⁱ Hydrochloric acid is sometimes used, but is much less damaging.ⁱⁱⁱ Concentrated solutions of strongly alkaline materials including sodium hydroxide can also be used.

Although chemical attacks occur all over the world, the UK has one of the highest rates of chemical attacks per capita in the world, according to Acid Survivors Trust International (ASTI).^{iv} From 2011 to 2016 there were 1,464 crimes involving a corrosive substance in London.^{iv} Work by the UK government to reduce the frequency of attacks is ongoing but this is unlikely to prevent their occurrence completely, therefore the need for a suitable neutralising system is required.⁵

Current recommended first-aid advice suggests flooding the exposed areas with water for at least 20 minutes and transfer to a hospital for further treatment.^v General first-aid advice recommends first-responders do not attempt to neutralise burns as the time taken to identify the corrosive and

an appropriate antidote would facilitate further damage compared to dilution with water.^v Water does not provide a neutralising mechanism for acid or alkaline materials; it remedies the burn by dilution and mechanical action removing the corrosive from the afflicted area.^{vi} It is possible to use weak acids such as 5% acetic acid to neutralise alkaline burns, whereas acid burns can use dilute solutions of weak sodium bicarbonate.^{vii} However, there are concerns over the enthalpy of reaction associated with these neutralisation processes causing secondary thermal burns.^{vii} Also, these treatments would have to be kept separate and identification of the corrosive would be required before selecting an appropriate treatment. This suggests a treatment system for chemical attacks needs to be amphoteric.

Other materials have similar potential advantages, however their application requires application within the first minute of exposure to a corrosive.^{vi} This target would be difficult to achieve given average response times for category 1 (life threatening) emergency calls is 7 minutes in the UK.^{viii} This suggests there is still a need for development of an amphoteric neutralising agent that can be effective in the average first-responder response times

The current study aimed to trial aqueous formulations developed from modified tree saps with biodegradable and non-toxic properties, referred to as sap-formulation A and sap-formulation B, as a counter to an attack with corrosive substances. These formulations have been shown to neutralise both acids, alkalis and chemical oxidisers, and demonstrate potential to be an effective tool for first responders when called to an attack.

2 Methodology

Sap-formulation A and B were formulated by Hydro Navitas Ltd. Dilution of sap-formulation A and sap-formulation B to a 10% v/v solution was achieved by adding the agent to water under magnetic stirring. 50% v/v sulfuric acid was prepared by adding 95% sulfuric acid to water under constant magnetic stirring with the receiver flask in a cold-water bath. 30% w/v sodium hydroxide and saturated sodium bicarbonate solutions were prepared by the same method.

2.1 pH Titrations

25 ml of a corrosive substance were pipetted into an insulated flask. The pH and temperature were recorded using separate probes: Mettler-Toledo Multi Seven, and Fisher Scientific ECOTEMP respectively. The pH probe was calibrated using standard pH 1.2, 4 and 7 buffers for acidic corrosives and pH 4, 7 and 9.22 for alkaline corrosives. The temperature probe was encased in glass filled with glycerol. The neutralising agent was dispensed in small aliquots from a burette and magnetically stirred for 5 seconds; a probe reading was taken after 60 seconds.

2.2 Residual Free-Cl₂ Titrations

Aliquots of sodium hypochlorite (technical grade) were neutralised with the theoretical quantity of neutraliser required to reach the equivalence point of the treatment. A 25 ml sample of treated sodium hypochlorite was pipetted into a 250 ml volumetric flask (dilution factor 10). A 5 g sample was taken and diluted with 50 ml of deionised water, 10 ml of 50% v/v acetic acid solution and 2-3g of potassium iodide were added. The solution was titrated against 0.1M sodium thiosulfate in the presence of a starch indicator. The oxidising capacity of the bleach was quoted as grams Cl₂ per litre of bleach solution.

2.3 Preparation of Pickled Sheepskins

Salted sheepskins (Buitelaar, IRL) were beamhouse processed to the pickled stage. The sheepskins were depickled, sammed and cut into 2.5 x 2.5 x 0.1 cm samples using a hydraulic clicking press (CPR, F60).

2.4 Sheepskin Chemical Burn Trials

Pelt sections were exposed to 2 ml of corrosive for 5 seconds to 1 hour after which, the sample was washed in 100 ml of treatment for 2 minutes. Samples were transferred to a vial containing 20 ml of buffered formaldehyde solution (3.8% v/v formaldehyde, 2.30 g l⁻¹ Na₂HPO₄, 8.73g l⁻¹ KH₂PO₄).

2.5 Scanning Electron Microscope Sample Preparation

Formaldehyde-preserved samples were submersed in acetone for 1 hour. The acetone was replaced with clean acetone for a further 30 minutes. The acetone was drained, and the samples dried for 12 hours. The samples were submersed in molten camphene (Sigma Aldrich, 50 °C) for 12 hours in sealed containers. Excess camphene was discarded, and the samples were refrigerated at 3 °C for 1 hour. The hardened samples were sectioned in the direction of the hair follicle crosssection the using a clean razor blade. Specimens were left in open air at room temperature for camphene sublimation for 12 hours. Specimens were then mounted using adhesive carbon pads (Agar Scientific). The samples were gold-coated using a Quorum Technologies SC7620 sputter coater.

2.6 Scanning Electron Microscope Procedure

Specimens were imaged by scanning electron microscopy (Hitachi, SEM-3000N).

2.7 Preparation of Raw Pigskins

Salted pigskins (DEVRO, UK) were washed and degreased at 35 °C (Trumpler, Pastasol BZ, Pastasol F). Skins were shaved using an electric hair clipper set to 1 mm. Shaved skins were cut into 75 x 200 mm samples and stored at 3 °C.

2.8 Pigskin Corrosive Burn Trials

4 ml of corrosive substance was dispensed over the pelt surface from an auto pipette (Socorex 1-10 µl). The corrosion process was recorded using a Nikon D7000 with an 18-200 mm f/3.5-5.6 lens at 200 mm, f/8 and a focal distance of 1 m. Photographs were also taken with a thermal imaging camera (FLIR, i7) throughout recording. After an exposure time of either 30 seconds or 5 minutes, the skin was neutralised.

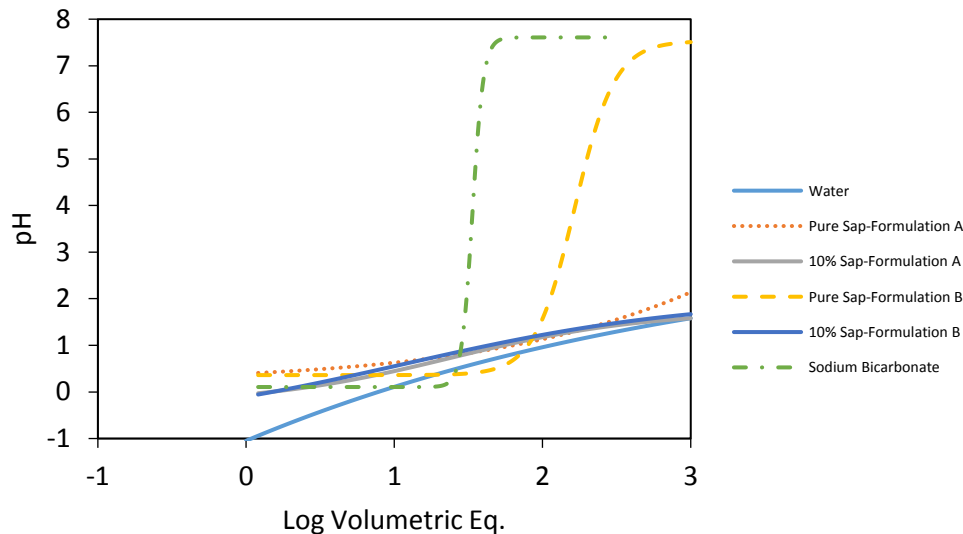
2.9 Pig skin and Sheepskin Volatiles Contents

A 2 x 2 cm sample of pigskin or sheepskin was accurately weighed and was dried in an oven (Abinghurst, UK) at 102 ± 2 °C for 12-16 hours. The samples were weighed and returned to the oven at the same temperature for one hour. The process was repeated until the sample weight remained constant. Volatile matter content was carried out in accordance with BS EN ISO 4684, and it has been assumed that the volatile matter content is equivalent to the moisture content.

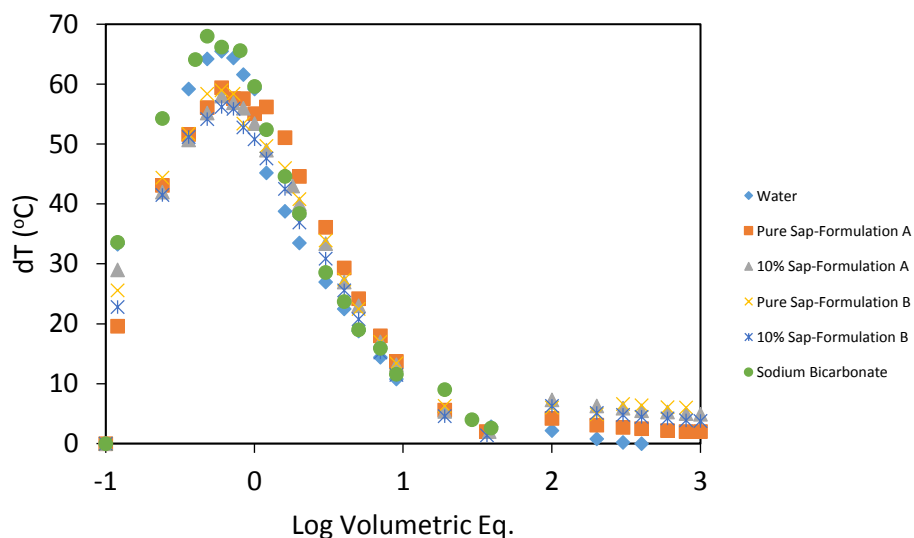
3 Results and Discussion

3.1 pH Titrations: Neutralising Agent into Corrosive

Figures 1 A and B show the pH and temperature profiles respectively of the neutralisation of 95% sulfuric acid. Diluted sap-formulation and water did not neutralise sulfuric acid within addition of 1000 volumetric equivalents of the neutralising agent. sap-formulation B and saturated sodium bicarbonate solutions show neutralising capability requiring 165 and 34 volumetric equivalents respectively.



A



B

Figure 1. pH (A) and temperature (B) profiles of 95% sulfuric acid during neutralisation as a function of volume of neutralising agent. X-axes are equivalent for cross-referencing.

The temperature increase is a result of hydration of the concentrated acid when an aqueous solution or water is added.^{ix} All neutralising systems were found to dissipate the resultant heat of hydration equally with 10 volumetric equivalents required to bring the change in temperature down

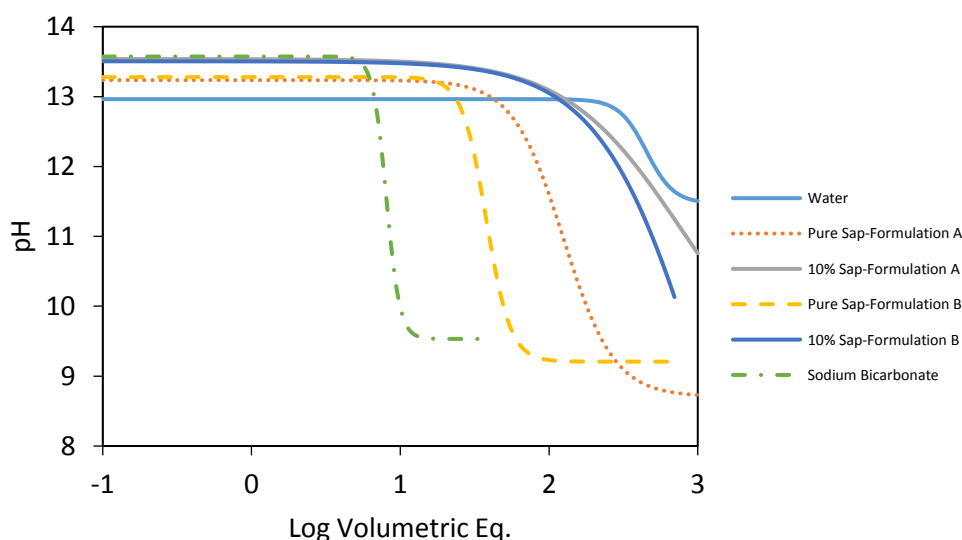
to +10 °C. This temperature change would equate to a real temperature of 35-40 °C, which is below the denaturation temperature of raw skin. Water and the saturated sodium bicarbonate solution reached peak temperatures of 7-9 °C greater than the sap-formulations.

Figure 1 demonstrates sap-formulation B and sodium bicarbonate neutralise strong acids, however, sodium bicarbonate reacts very violently with strong acids with rapid evolution of CO₂ and excess heat of neutralisation (typically 50 to 60 kJ mol⁻¹).^x Sodium bicarbonate solutions also have a limited shelf life, as decomposition into CO₂ and water occurs.^{x,xi} The key benefit of the sap-formulation B is the ability to neutralise strong acids without a violent reaction or significant evolution of neutralisation heat, and a long shelf life. The obvious advantage of sap-formulation B compared to water is the capacity to neutralise a strong acid, whereas, water solely functions by a dilution mechanism.

The pH and temperature profiles of 30% (w/v) sodium hydroxide, as shown in **Figure 2**, illustrate diluted sap-formulations and water did not neutralise within an addition of 1000 volumetric equivalents. The concentrated sap-formulations and saturated sodium bicarbonate show neutralising capability requiring 125 (sap-formulation A), 38 (sap-formulation B), and 8 volumetric equivalents respectively.

All neutralising systems were found to dissipate the resultant heat of hydration equally. The peak temperature changes recorded were 2°C therefore, heat dissipation not a significant concern for sodium hydroxide solutions. The exception to this is the saturated sodium bicarbonate system with a peak change of 6°C, which is likely to be due to the heat of neutralisation, however this change is still regarded as insignificant.

Both sap-formulations neutralise strong alkaline substances, but are not as efficient as a saturated sodium bicarbonate. However, due to the violent reaction between sodium bicarbonate and sulfuric acid, and the requirement for an amphoteric neutralising agent, sap-formulation B has the potential to be a suitable alternative to sodium bicarbonate.^{xii} The advantage of the sap-formulations compared to water is the capacity to neutralise a strong alkaline. Water does not have this capacity and solely functions by a dilution mechanism. Sap-formulation B presents an amphoteric behaviour, which is a fundamental characteristic of any single component treatment system. Although sodium bicarbonate is also amphoteric, the severity of the reaction with strong acids would mean identification of the corrosive during a chemical attack may be required.



A

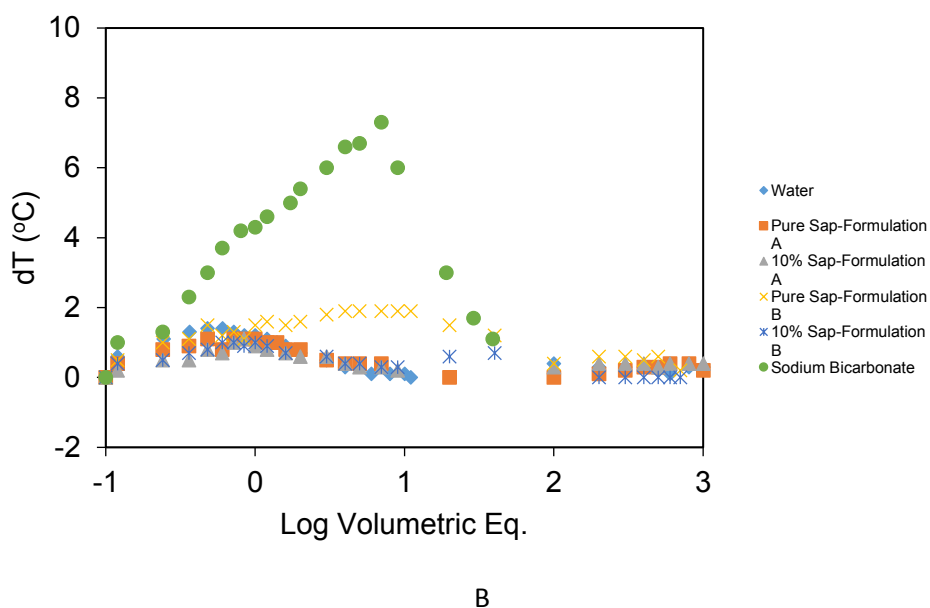


Figure 2. pH (A) and temperature (B) profiles of 30% (w/v) sodium hydroxide during neutralisation as a function of volume of neutralising agent.

3.2 Residual Sodium Hypochlorite Reduction Titrations

As alkaline pH, bleach formulations containing sodium hypochlorite also have an oxidising potential that requires neutralisation to prevent damage to skin in an attack situation.^x Agents capable of neutralising pH may not reduce oxidising agents, therefore, the residual free Cl_2 of pH neutralised sodium hypochlorite was analysed, as shown in **figure 3**. 1000 volumetric equivalents of water were used for the water reference, as no equivalence point was observed.

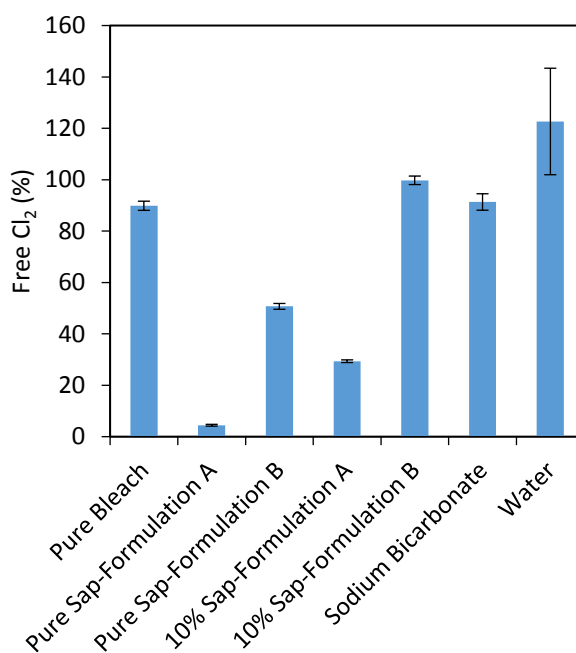


Figure 3. The free Cl_2 concentrations of pH neutralised sodium hypochlorite solutions.

Both sap-formulations can reduce significant quantities of the available free Cl_2 with sap-formulation A reducing 95% of the available free Cl_2 . Diluted sap-formulation B, saturated sodium bicarbonate and water do not have any significant reducing capacity. Sap-formulation B was expected to show more significant reducing properties compared to sap-formulation A, as sap-formulation B was more efficient at neutralising pH, however, this was not observed. The chemical composition of sap-formulation B and sap-formulation A are not publicly known, and it is not possible to explicitly attribute the difference in bleach reducing properties. Water does not reduce sodium hypochlorite and only acts through dilution mechanisms.

3.3 Chemical Attack Trials

Sections of beamhouse-processed sheepskins were exposed to corrosives for different timed periods and neutralised by submersion into a neutralising agent. Scanning electron microscopy (SEM) was used to assess the skin structure and damage. **Figure 4 A** is a micrograph of the complete cross-section of an undamaged control sample showing the presence of: hair follicles blood vessels, sweat glands, and cavities due to the removal of fat within the skin cross-section.^{xiii} **Figure 4 B** shows scanning electron micrographs of a full cross-section of sheepskin exposed to 95% sulfuric acid for 5 seconds prior to neutralisation in a pure sap-formulation A solution showing a complete collapse of the inherent collagen fibre structure. There was no evidence of hair follicles, blood vessels, sweat glands or cavities in the upper (grain) section and no evidence of the inherent fibre structure in the lower (corium) sections. This observation was made for all neutralisers tested after a 5-second exposure to 95% sulfuric acid.

Figure 4 C displays scanning electron micrographs of a cross-section of sheepskin exposed to 95% sulfuric acid for 5 seconds prior to neutralisation in a saturated sodium bicarbonate solution and shows inherent fibre structure in the middle of the cross-section. However significant damage to the upper (grain) and lower (corium) sections was evident. Damage to lower corium has been attributed to some of the 95% sulfuric acid contacting the underside of the sample in error. More significantly it provides evidence the rate of neutralisation between 95% sulfuric acid and saturated sodium bicarbonate is faster than the sap-formulations. **Figure 4 C** also indicates the presence of spherical cavities in the grain and lower corium sections. A postulated cause for this observation is the reaction mechanism between sulfuric acid and sodium bicarbonate which, results in the evolution of gaseous CO_2 .^x It is possible neutralisation is occurring within the skin cross-section and releasing trapped CO_2 , which could expand the surrounding fibre matrix leaving a spherical cavity upon release of the trapped CO_2 . Sodium bicarbonate was the only neutralising agent to demonstrate this behaviour and highlights a potential issue with its application as a pH treatment in an chemical attack scenario. The sap-formulations do foam during the neutralisation of sulfuric acid; however, the reaction is significantly less vigorous compared to sodium bicarbonate and damage like sodium bicarbonate was not observed.

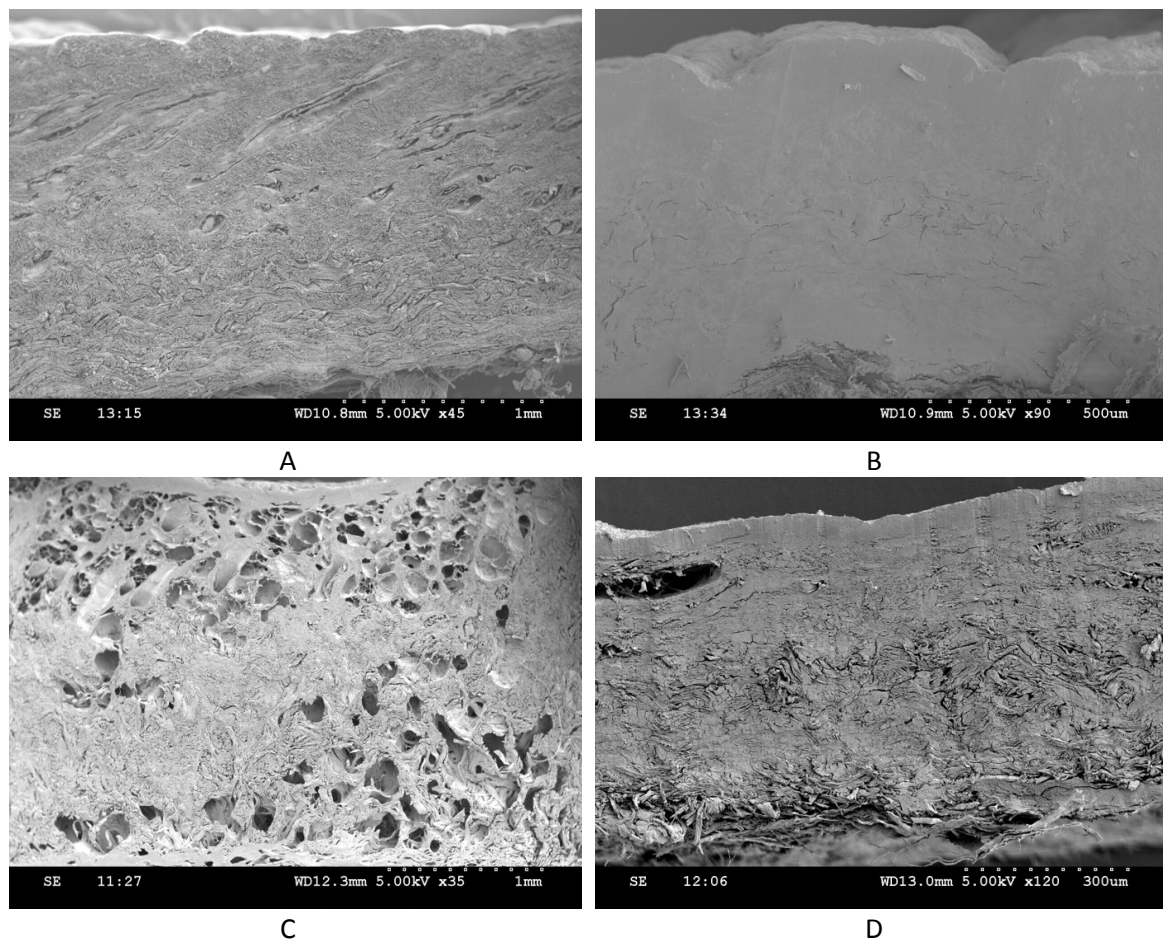


Figure 4. Scanning electron micrographs of neutralised sheepskin cross-sections: Undamaged (A) 5s exposure to 95% sulfuric acid (B) 5s exposure to 95% sulfuric acid neutralised with sodium bicarbonate (C) 1-hour exposure to sodium hypochlorite (D).

The reaction between sodium hypochlorite and collagen is significantly slower compared to 95% sulfuric acid and 30% sodium hydroxide, as significant parts of the inherent fibre structure was still evident after a 1-hour exposure and neutralisation with sap-formulation B, as shown in **figure 4 D**. In all cases, only limited collapse of the fibre structure, was observed within 1 hour of exposure to sodium hypochlorite, thus suggesting dermal and corium layers of the skin cross-section have intrinsic resistance to hydrolytic damage. **Figure 4 D** show the upper most layer has completely collapsed showing no inherent fibre structure. In all cases, the presence of a neutralising agent does not reverse the damage cause to the sub-epidermal layers. Although significant parts of the inherent fibre structure are observable, the sodium hypochlorite solution does cause damage. This damage will be imparted via an alkaline hydrolysis mechanism analogous to sodium hydroxide, but significantly slower due to a lower solution pH. Under the current methodology, damage caused by the oxidative capacity of sodium hypochlorite cannot be differentiated against the damage caused by alkalinity. However, it is suspected not to be significant, as the overall damage observed is limited compared to sulfuric acid. Exposing sheepskin to sodium hydroxide resulted in comparable observations to the effect of 95% sulfuric acid.

Topographical thermographs were taken using a thermal imaging camera to compare an unexposed area of a skin sample with an exposed area. **Figure 5** is an example of an unexposed section of pigskin. **Figure 5 B-D** are thermographs showing the increase in temperature around the burn area during exposure and after neutralisation of 95% sulfuric acid. **Figure 5 B** confirms the

immediacy of the exothermic dehydration reaction, however the observed increase in temperature was not as significant as suggested by the titrations reported earlier. This may be a consequence of the moisture and fat content of the skin. The heat observed upon exposure of the skin to sulfuric acid is a consequence of the reaction between sulfuric acid and the skin's water content. The moisture content of the pigskins used for these trials was 58-60 %, which qualitatively matched the moisture content of living skin tissue. It would be expected, skin samples with a lower moisture content would show a lower maximum temperature, whereas skin samples with a higher moisture content would be expected to have a higher maximum temperature upon exposure to sulfuric acid. The maximum temperature observed during pigskin trials involving sulfuric acid was 40 °C. **Figure 5 C** confirms the heat of dehydration is still evident after 5 minutes of exposure, however the maximum temperature was below 30 °C, thus suggesting heat dissipation to the surroundings occurred and the dehydration reaction has significantly slowed down.

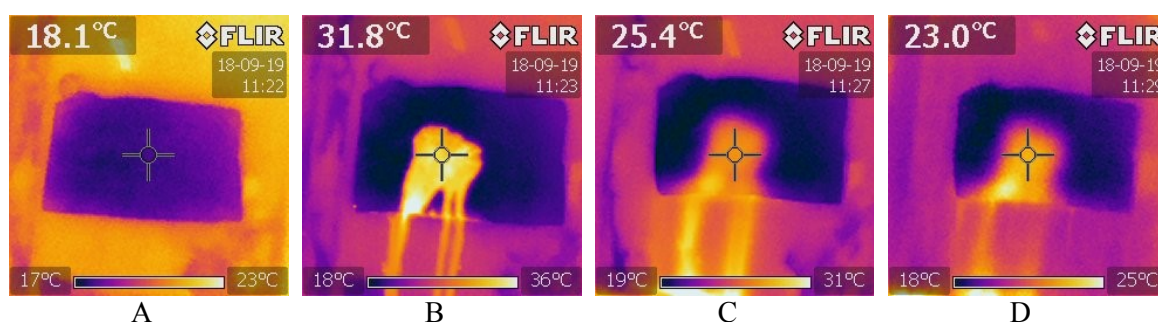


Figure 5. Thermographs of pigskin exposed to 95% sulfuric acid for 5 minutes and neutralised with sap-formulation A: before exposure (A) at exposure (B) after 5 minutes exposure (C) 1 minute after neutralisation (D).

Figure 5 D is a thermal photograph taken 1 minute after neutralisation by aspirating pure sap-formulation A over the burn area. The burn area is still distinguishable, but the maximum temperature observed was less than 25 °C. During neutralisation, there was no observable rise in temperature due to the enthalpy of neutralisation, which suggests the benefits of a neutralising mechanism are not compromised by a temperature increase due to the thermodynamics of neutralisation. This observation is significant, as it demonstrates a fundamental advantage compared to using water as a neutralising agent. The above observations apply to all neutralising agents being tested for 30-second and 5-minute exposure times. All trials involving 30% sodium hydroxide showed no significant change in skin temperature during exposure or neutralisation. This observation also applied to the trials involving sodium hypochlorite, which agree with the titrations mentioned earlier.

In addition to chemical burns caused by the initial exposure, it is possible for further skin damage to occur from long-term incomplete neutralisation; these are referred to as secondary burns. The application of pH treatments in the case of a chemical attack scenario should consider the mitigating properties against secondary burns as well as their effect on the immediate, primary burns. **Figure 6** compares the burn areas of pigskin exposed to 95% sulfuric for 20 seconds and neutralised with: water (A & D), sap-formulation B (B & E) and saturated sodium bicarbonate solution (C & F) 4 hours after neutralisation.

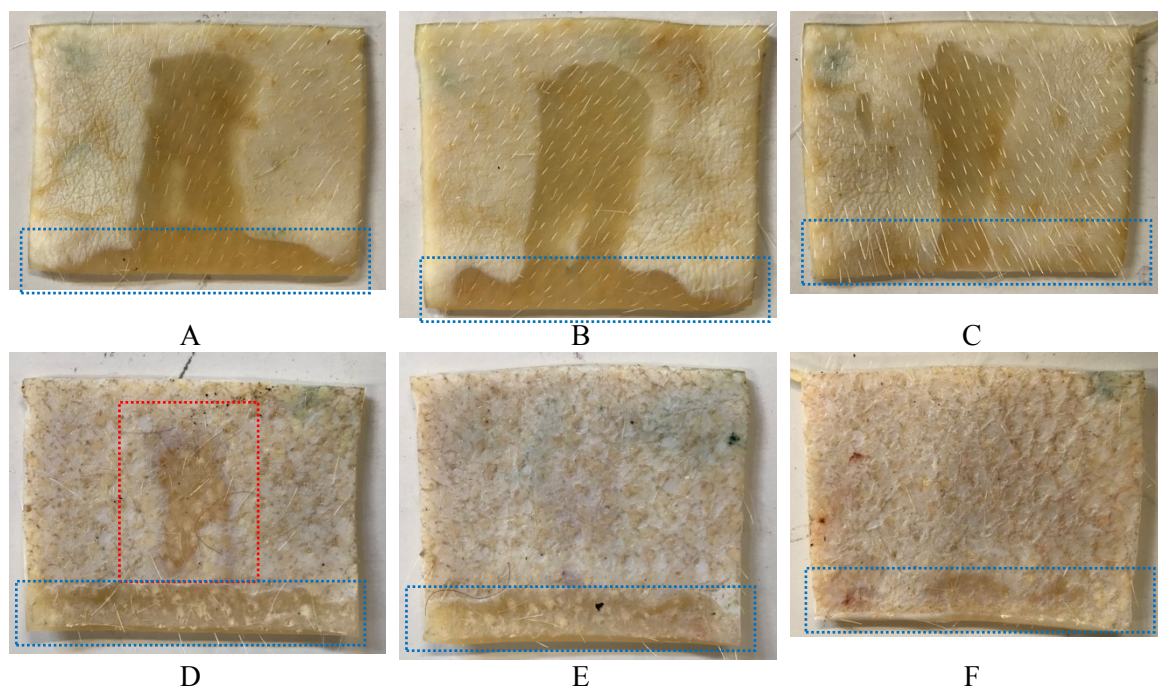


Figure 6. Photographs showing secondary burns 4 hours after neutralisation with a range of agents: Water topside (A), water underside (D), sap-formulation B topside (B), sap-formulation B underside (E), Sodium bicarbonate topside (C), sodium bicarbonate underside (F)

Figure 6 D shows a clear secondary burn has developed on the underside of the skin sample neutralised using water, highlighted in red. In comparison, the skin samples neutralised with sodium bicarbonate and sap-Formulation B did not develop a secondary burn on the underside within the same timeframe. This is a significant observation, as it provides evidence sap-formulation B and sodium bicarbonate can mitigate against secondary burns. The areas highlighted in blue appear on both sides of all 3 samples and are edge effects caused by sulfuric acid encountering the underside of the sample and burning from underneath: edge effects should not be considered when reviewing secondary burns.

4 Conclusions

The amphoteric formulations, based on natural products, have been shown to be efficacious in treating acid, alkali and oxidising attacks: they do not exhibit the disadvantages of pure water or bicarbonate solution. Therefore, they could be used by first responders, who can safely use the solutions *ad lib.* without fear of causing more harm. Similarly, the products can be carried by the police and fire services; moreover, they can be held by organisations or institutions where there is a perceived risk of attack, such as night clubs.

References

1. L. M. Taylor, *Ga. Journal Int'l & Comp. Law.*, 2000, 29, 395–419.
2. M. Bandyopadhyay, M. R. Khan, in: *Violence against women in Asian societies*, Routledge Curzon, Abingdon, Editors: L. Manderson and L. R. Benjnett, 2003, Chapter: Loss of face: Violence against women in South Asia, 61-75
3. J. Welsh, *It was like burning in hell: A comprehensive exploration of acid attack violence*, Carolina Papers on International Health, Center for Global Initiatives, University of North Carolina, 2006
4. <http://www.asti.org.uk/a-worldwide-problem.html> [Accessed Oct 2018]
5. <https://www.sja.org.uk/sja/what-we-do/latest-news/first-aid-for-acid-attacks.aspx> [Accessed Oct 2018]
6. *Diphoterine® Solution: Captures the Corrosive and Eliminates it*, Prevor, www.prevor.com [Accessed Oct 2018]
7. K. L. Andrews, A. Mowlavi, S. M. Milner, *Plast. Reconstr. Surg.*, 2003, 111, 1918-21.
8. <http://www.qualitywatch.org.uk/indicator/ambulance-response-times> [Accessed Oct 2018]
9. G. Hill, J. Holman, *Chemistry in Context*, ITP, Surrey, 4th Ed., 1995, Ch. 23, 360 -380
10. E. N. Ramsden, *A-level Chemistry*, Thornes Publisher, Cheltenham, Illustrated edition, 1985, Ch. 18, 352
11. <http://www.td-bkh.ru/en/products/35> [Accessed Oct 2018]
12. J. S. Fordtrana, S. G. Morawski, C. A. Santa Ana, F. C. Rector Jr., *Gastroenterology*, 1984, 87, 1014–1021
13. A. D. Covington, *Tanning Chemistry: The Science of Leather*, RSC Publishing, Cambridge, 1st Ed., 2009, Ch 2, 29 - 71