Chapter

Ancient and Contemporary Industries Based on Alkali and Alkali-Earth Salts and Hydroxides: The Historical and Technological Review

Rina Wasserman

Abstract

Although sodium, potassium, calcium, and magnesium were isolated *as the chemical elements* by Sir Humphry Davy for the first time at the beginning of the 19th century, alkali salts and hydroxides have been widely known and used since the very ancient time. The word "alcali" & "alkali" was borrowed in the 14th century by literary Roman-Germanic languages from Arabic *al-qalī*, *al-qâly* ou *al-qalawi* (القَلْوي), which means "calcinated ashes" of saltwort plants. These ashes are characterized nowadays as mildly basic. They have been widely used in therapy, cosmetics, and pharmacy in Mediaeval Europe and the Middle East. However, the consumption of these alkali containing ashes, as well as natron salts and calcined lime-based materials used for different customer purposes, like therapy, pharmacy, cosmetics, glass making, textile treating, dyes, brick making, binding materials, etc., was commonly known since the very ancient times. The current review of the archeological, historical, and technological data provides the readers with the scope of the different everyday life applications of alkali and alkali-earth salts and hydroxides from ancient times till nowadays. The review obviously reveals that many modern chemical manufacturing processes using alkali and alkali-earth salts and hydroxides have a very ancient history. In contrast, there has been a similarity of targets for implementing alkali and alkali-earth salts and hydroxides in everyday life, from the ancient past till the modern period. These processes are ceramic and glass making, binding materials in construction, textile treatment, metallurgy, etc. So, this review approves the common statement: "The Past is a clue for the Future."

Keywords: alkali, caustic, lime, pH, natural cement, Portland cement

1. Introduction

The alkali metals Na and K reside in the first column of the periodic table. Sir Humphry Davy, a prominent English scientist of the 19th century, electrolyzed sodium, Na, and potassium, K, and named them in 1807 [1]. At first, Davy called metallic potassium and sodium "the basis of potash" and "basis of soda," respectively. Consistently, he renamed these new metals potassium and sodium. Dmitry Mendeleev designated this discovery as " … one of the greatest discoveries in Chemistry … " [2]. However, after discovering these alkali elements that play an essential role in modern life, they have been little known by non-scientists for many years [3]. Although potassium and sodium as metals entered human life only ca. 200 years ago, humans have been familiar with their substances for thousands of years. Usage, treatment, and conscious transformations of alkali substances, which are almost six thousand years old, could be called the first advanced chemical technology in humankind's Big history.

The word "alcali" & "alkali" was borrowed in the 14th century by literary Roman-Germanic languages from Arabic al-qalī, al-qâly ou al-qalawi (القلوي), which means "calcinated ashes" of saltwort plants. These ashes are chemically characterized nowadays as mildly basic. They have been widely used in therapy, cosmetics, and pharmacy in Mediaeval Europe and the Middle East. However, the consumption of these alkali containing ashes, as well as natron salts and calcined lime-based materials used for different customer purposes, like therapy, pharmacy, cosmetics, glass making, textile treating, dyes, brick making, binding materials, etc., was commonly known since the very ancient times.

The current article intends to review those technological processes of alkali substances, modernly called 'chemical technology,' and track these processes' ancient and historical roots revealed by archeological findings and historical descriptions.

Undoubtedly, the ancient civilizations were not aware of the contemporary "chemical language" and did not carry out any scientific investigations or testing the chemical and technological procedures before their implementation. However, the archeological findings have revealed in the last 100 years a vast amount of built-in chemical knowledge possed by the prominent ancient civilizations in their everyday life. Alkali salts played an essential role in human health and body care during ancient times. The ancient texts' interpretations have revealed alkalis substances' conscious usage as detergent and hygienic remedy throughout human history. Furthermore, the ancient texts have distinguished between alkaline salts' mineral and botanical origin, although emphasizing similar usage. Let us get down to some examples of alkali-based substances' knowledge and use in ancient and historical times.

2. Use of alkaline salts in ancient and historic cosmetics, food, cleaning, and medicine

2.1 Alkaline salts as the most initial raw materials of the ancient Mesopotamian pharmacology

The first documented use of ordinary table salt and soda could be related to Sumer and Akkadian Empires in Mesopotamia (3500–2000 BCE). **Figure 1** presents the map of the ancient Near East in the fourth millennium DC. At the beginning of the 20th century, the University Museum's archeological expedition, Philadelphia, the USA, to Nippur (a lower part of modern Iraq) excavated the cuneiform tablet aged ca. 2100 BCE [5]. In the tablet (**Figure 2**) decrypted at the half of the 20th century, the Sumerian script described the pharmacological processes involving alkaline substances of mineral and botanical origin. The mineral salts of alkali metals mentioned in the tablet are sodium chloride and potassium nitrate. Sumerians obtained alkalis also from soda ash, which they called Td-Gaz. This soda ash had a botanical origin by burning halophytic (high salinity) and alkaline plants, like glassworts (most likely the *Salicornia fruticosa* L.) rich in sodium carbonate, Na_2CO_3

Figure 1.
Map of ancient Mesopotamia [4].

[5, 7]. Sumerians had an abundance of designations for these alkaline plants and alkali ashes and salts according to their origin and manufacturing processes [8–10]:

- *di-ni-ig*: potash; salt (dè, 'ashes', + nağa, 'potash')
- *nağa*: potash, K_2CO_3, soap;
- *nağa-Gaz*: crushed soda (plant?) ('soda, alkali' + 'to crush, to grind, to grate, powder');
- *nağa-si-è*: sprouted alkaline plant ('soapwort' + 'antennae' + 'to go forth');
- *ne-mur*: glowing coals, fire, alkali, potash; ashes; charcoal ("tree" + compound verb verbal element)

Glassworts are hardy to high alkaline environments and store absorbed alkaline salts in their tissues during growth [11–13]. According to the modern analytical tests, sodium and potassium carbonate content in ashes obtained from the Near East halophytic plants could be 38.5% - 93% [11]. According to the Sumerian script, the further treatment of soda ash included its multistage purification and pulverization processes. Sumerians widely implemented this "halophytic ash" soda in pharmacology, making simple detergents and soaps for body cleansing and religious purifying:

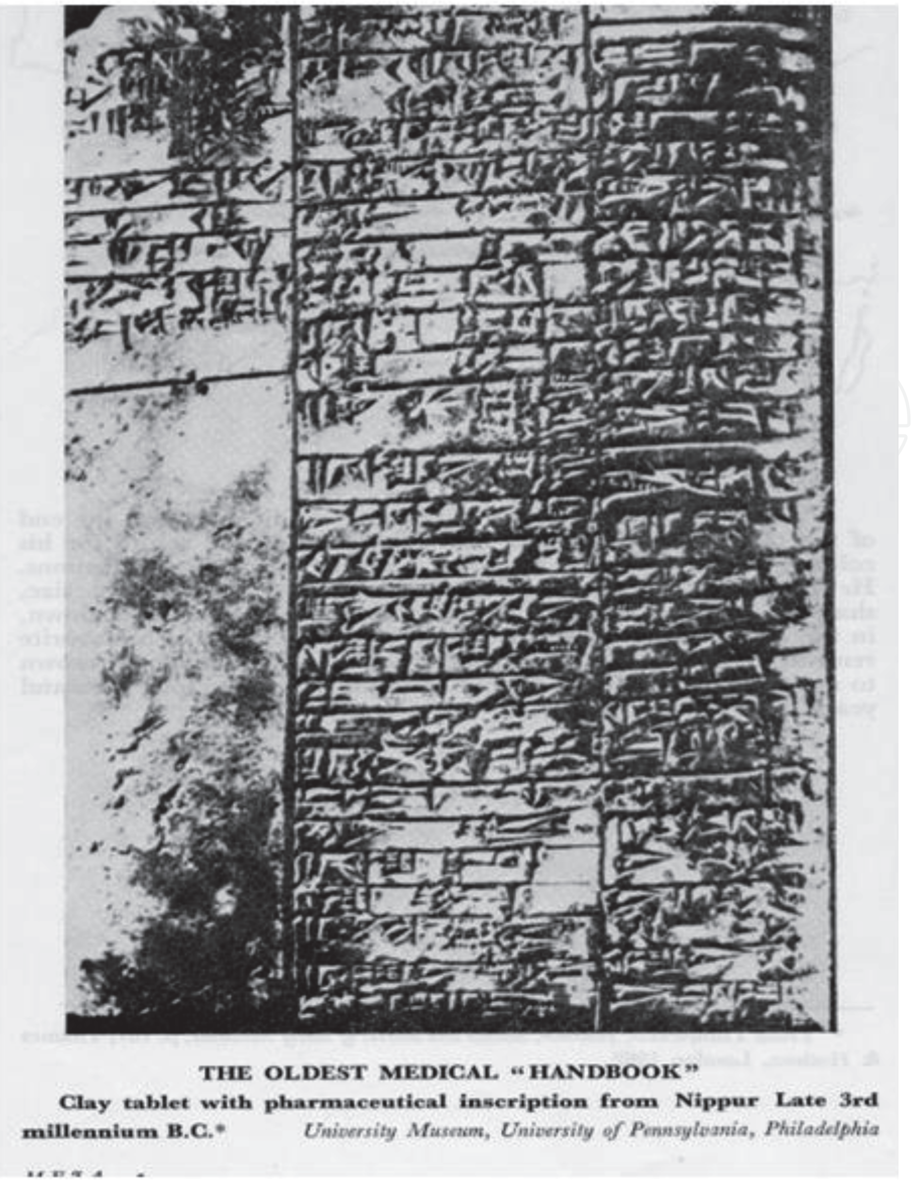


Figure 2.
Picture of cuneiform (clay tablet) with the pharmacological inscription, Nippur, c. 2100 B.C. University of Pennsylvania, Philadelphia USA. [6].

"With water I bathed myself. With soda I cleansed myself. With soda from a shiny basin I purified myself." [14].

2.1.1 The rise of soapmaking

Another Sumerians' pharmacological use of sodium salts (soda ash and regular salt, NaCl) was making a medicated ointment soap as a rubbing remedy for ailments. The preparation process was based on thorough mixing of sodium salts, i.e., sodium ash and regular salt, with various natural organic ingredients. [7]. Generally, the earliest Sumerians' soaps were made for medical purposes and wool washing but not for general cleansing purposes. To extract alkali from the plants, Sumerians put into use the following technological stages [14]:

- slow combustion or incineration of the dried halophytic and alkaline plants;
- leaching or washing of the plant ash;

- separating the mixture by water evaporation and drying until the salt cake crystallizes on the vessel's sides;

- calcination of the crude product to ignite organic substances.

This method was based on a long-time, slow and thorough process to assure the high yield of alkalis' extraction and, therefore, the more expensive product was obtained. The Sumerian elites used this product for ritual purifying. Common Sumerians got a more simple leaching process in everyday life. They stirred the plant ash in water and filtered the suspension before using it to remove the insoluble impurities. The resulting basic lixivium (alkali leachate) was widely used for everyday cleansing and washing purposes.

2.1.2 Advanced technologies for table salt manufacturing

The Old and New Babylonian languages, which are Sumerian and Akkadian, respectively, used the same logogram for table salt , [9, 10, 15], but had the different pronunciation of this term: *mu-n*(u) in Sumerian (Old Babylonian) vs. *ṭab-tu(m)* in Akkadian (New Babylonian) [8, 16].

Table salt, which is sodium chloride, NaCl, is described in the decrypted Sumerian (Old Babylonian) texts as an essential ingredient of the human's diet, food preservative, and the pharmacological salting-out ingredient to separate a medicated ointment soap from the glycerin, excess of water, and impurities [7, 14, 17, 18].

A great deal of salt treatment in various parts of the Ancient World, since the prehistoric times, till the 19th century C.E., was the uniformity of salt production techniques [19]:

a. Rock salt was mined or gathered.

b. Seawater and brine were universally used to remove salt by natural evaporation or artificial solution boiling, respectively.

c. Halophytic plant ashes were washed and refined.

d. Salt molds from different places worldwide were based on very similar ceramic vessels.

The utilization of salines for salt production was probably the most crucial method of salt superiority in antiquity. The leather sacks were used in Ancient Mesopotamia to transport large quantities of salt from salines to villages and towns. Also, salt molds made of porous ceramic material or reeds were used to transport the precipitated "salt cakes" to consumers grinding them for daily use. Wooden bowls served as salt containers in the home [17]. In the Sumerian and Akkadian Empires, salt served as a reward for work as a state servant. According to the decrypted Akkadian texts, unskilled workers and high-quality artisans employed at the reconstruction of the Ékur Temple (**Figure 3**) in Nippur under the Kings Naram-Sin (reigned 2261–2224 BCE) and Shar-Kali-Sharri (ruled 2217–2193 BCE) were given 0.421 and 0.842 liters of salt per capita per month, respectively [20].

Those amounts' mass equivalent comprises an average of 10.4 and 20.8 gr salt per person per day in a 30-day month, respectively [17]. According to the U.S. Food and Drug Administration, the recommended daily sodium intake is less than

Figure 3.
Photograph of Ekur, the ziggurat of Enlil at Nippur [4].

2,300 mg per day [21]. In the context of salt intake, one gram of sodium equals approximately 2.5 gr of salt [22]. Thus, by present-day measurement, the ancient Accadian workers obtained a surplus of salt as salary. Perhaps, this was done because of the extensive use of salt as an animal food' preservative in a hot climate. Also, salt played a high role in many medical remedies to help afflictions of the soul, psyche, male virility, and magic rituals in the Ancient Sumer and Accadian empires [17]. Considering the Akkadian Empire's high population during the third millennium BCE, massive salt consumption could be imagined. Therefore, large-scale logistics of salt gathering, a well-established delivery system, massive salt loading and unloading operations, commodity distribution, and numerous material equipment could be considered for that ancient society [17].

2.1.3 Saltpeter green manufacturing

Another alkali substance described by Sumerians pharmacological text [5] was niter or saltpeter, K_2NO_3. Sumerians called saltpeter *mú-nu* (*mú*, 'to make grow,' + *nu*, 'fire'), whereas the Akkadian word for saltpeter was *marru* (bitter) [17]. Nevertheless, also, in this case, they used for this alkaline salt the same logogram  [10]. The Old Babylonian (Sumerian) word used for saltpeter in the 4th millennium DC demonstrates the knowledge of potassium nitrate ignitability. It should be emphasized that the last millennium civilization has begun using the saltpeter as the oxygenating ingredient in gunpowder only since 9th century AD [23, 24].

An exciting fact is that Sumerians and Assyrians obtained this salt by a crystalline formation from the surface drains containing nitrogenous urine waste products. This intermedial crystallized substance contained a mixture of alkali salts (sodium chloride, potassium nitrate, and others). According to this ancient script, Sumerians harnessed fractional crystallization processes to purify obtained niter. The text, although, emphasized the yield of the processes. Our days, we call such processes of 'green' innovative and emerging technologies [25–29].

2.2 Descendants of the knowledge and experience of sodium alkaline salts

The knowledge and experience of sodium alkaline salts' use were "inherited" by Babylon (2000–144 BCE) and the Hittite (1900–700 BCE) empires (both in Mesopotamia). Alkaline substances based on wood or plant ash were in high demand there. A ca.1300 BCE text described the Hittites using sodium salt, possibly sodium soda, and another alkali compound from plants, for washing the hands in a religious practice [14]. In ancient Babylonia, many halophytic plants were used for their alkaline substances. Babylonians used the same operations as Sumerians to extract alkalis from the plants for cleansing, hygienic, ritual, cosmetical, and medical purposes.

The usage of table salt, NaCl, as a food preservative agent was well known in ancient Mesopotamia in the first millennium BCE [18]. Table salt was an essential product in the food allowance paid by Ancient Mesopotamian rulers to workers and was considered a necessity for regular human maintenance.

2.3 Alkaline salts in the ancient Egyptian pharmacology (3000 BCE: 395 CE)

Another civilization distinguished by a conscious understanding of alkalis salts' importance and their broad medical and pharmacological usage was Ancient Egypt (3000 BCE – 395 CE). Alkalis salts used by the Egyptians since very ancient times were mineral soda (natron), $Na_2CO_3{\cdot}NaHCO_3{\cdot}xH_2O$, regular salt, NaCl, and sodium sulfate, Na_2SO_4 [30–32]. Natural Soda occurs in Egypt principally in the Wadi Natrun in the Libyan desert (**Figure 4**), and to less extent, at El Barnugi, in Lower Egypt, and at Mahamid, in Upper Egypt.

The Wadi Natrun deposits have been probably the oldest known source of natural soda globally, and they served to supply that commodity for thousands of

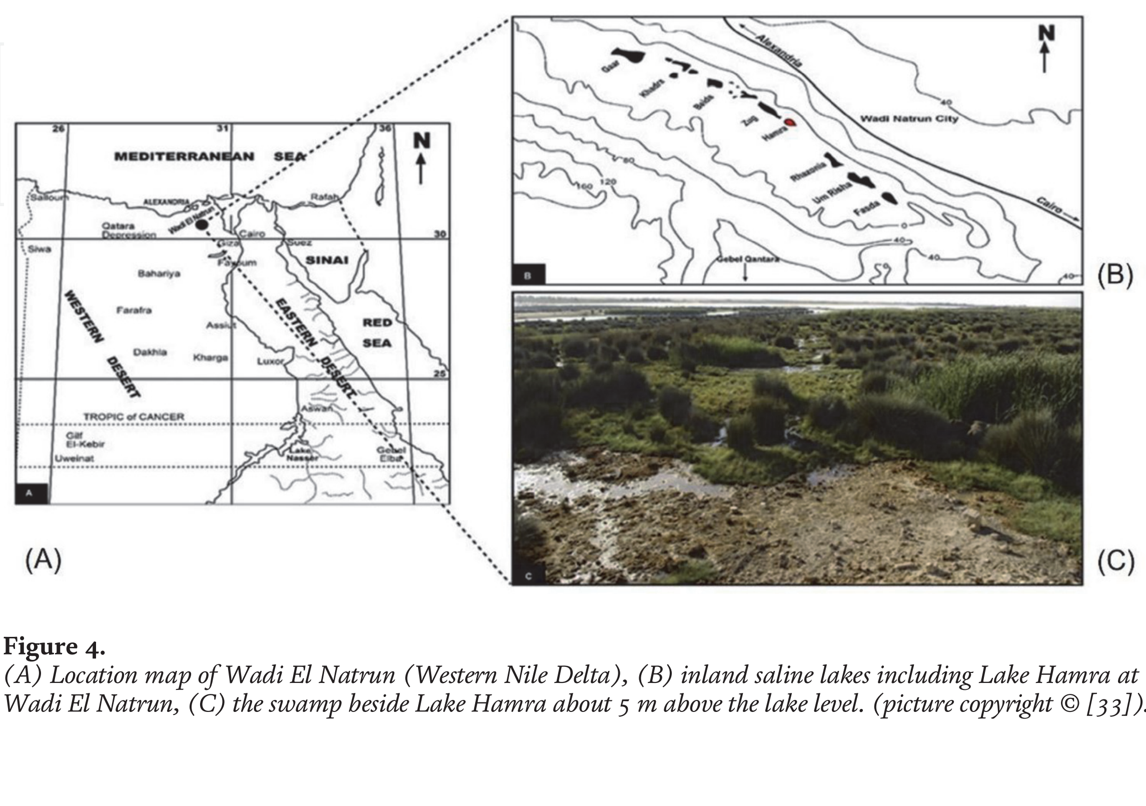


Figure 4.
(A) Location map of Wadi El Natrun (Western Nile Delta), (B) inland saline lakes including Lake Hamra at Wadi El Natrun, (C) the swamp beside Lake Hamra about 5 m above the lake level. (picture copyright © [33]).

years. In ancient times there were two soda lakes, which became united when water was most abundant [30]. The soda was found there in three forms:

a. as a solution in the lakes' water;

b. in a solid form at the bottom of the lakes;

c. as a crust on the ground.

The archeological excavations of the 19th and 20th centuries revealed (among others) seventeen ancient Egyptian papyri dealing with medical, pharmacological, and body purification issues and covering the period of more than two millennia, dating from the Middle Kingdom (2040–1640 BCE) to the end of the Greco-Roman Period (332 BCE-395 CE) until the Roman Empire's break up [34]. These papyri proved the importance of sodium salts in Ancient Egypt. However, sodium salts' usage in medicine, mummification, and ancient Egypt's hygiene began much earlier, five millennia ago, during the Early Dynastic Period (2920–2575 BCE) [31, 32].

The papyri mentioned plenty of times usage of sodium-based minerals as medication commodity:

a. salt from seven geographic origins. The salt, which is sodium chloride, was mentioned 175 times in total. The Egyptians could have potentially exploited the local salt from the Wadi Natrun and the Oasis of Siwa, harvested from salt pans in the Mediterranean and imported into Egypt from the Sinai Peninsula and some other sea salt works abroad [31].

b. natron from five geographic origins. The use of natron was described in papyri 92 times in total. The primary sources of natron within Ancient Egypt were the deposits at Wadi Natrun in the Lybian desert and El Kab in Upper Egypt south to Luxor. Ancient Egypt also imported natron from Sudan, Nubia, and Syria [31].

Furthermore, the salt and natron's mentions are more than one-third of the papyri's total mineral references. No other mineral was mentioned so frequently in the medical. These figures confirm the importance of sodium salts for health treatments in Ancient Egypt.

According to the papyri, the most common causes of salt usage in Ancient Egypt were treating wounds and mummifications (sodium chloride is well known as a putrefaction inhibitor), cure against diarrhea and dehydration, and cosmetics [31]. The interesting fact is that the use of salt is still quite common among traditional folk remedies.

In Ancient Egyptian medicine, natron's use was very similar to salt, mostly externally for wound treatments, skin curing, purification, mummification and embalming, and washing. M. Sapsford carried out the analytical tests to reveal and estimate salt and natron's role in the papyri's skin-curing prescriptions [31]. This study showed that salt served a moisture's retainer's role in anti-wrinkle skin creams, and natron possessed the highly desiccant ability. For the purification, salt and natron were used after an illness as a ritual cleansing means to be re-accepted as a fully functioning person in Ancient Egyptian society. Natron was also used as a means of unique purifying oneself after a period of "uncleanliness." There is some papyri' evidence of salt and natron' use for laundry' state-provided service. The exceptional importance of salt and natron for Ancient Egyptian society could be demonstrated by the fact that the village's households received a part of their monthly ration package by salt and natron [35].

2.4 Standard practices with alkaline salts adopted by ancient Hebrews, Greeks, and Romans (ca. 1150 BCE: 500 CE)

The Old Testament texts describe the wide use of salt by ancient Hebrews for a variety of purposes [36]:

a. sacrifices;

b. with food;

c. medicinal properties as an anti-infective agent;

d. as a symbol of the permanence of a covenant due to the observation that salt does not undergo decay;

e. as a symbol of perpetual desolation.

Ancient Hebrews distinguished between alkali sodas of different origins. They called natron, the mineral sodium carbonate, *neter*. In comparison, the word *borit* was used for sodium carbonate of vegetable origin (halophytic plant ash). The Ancient Hebrews commonly used *neter* and *borit* as laundry and body-cleaning agents [37].

The ancient Greeks and Romans eventually adopted these ancient practices of alkali salts' usage as laundering and body-cleaning agents and distributed them on the European continent [37]. However, since 600 BCE, the above-mentioned technological practices were changed to obtain solid soap, whereas wood ash became the main alkali-containing constituent, and animal fats were the binders in solid soaps. Pliny the Elder attributed the invention of alkali containing solid soap to one of the northern Celtic tribes [38]. Galen (129–199/216 CE), Greek physician, writer, and philosopher, wrote: "Soap is made by cooking beef, she-goat, or wether fat, mixed in with lye and quicklime." [39].

2.5 The Middle East as the disseminator of the ancient pharmacological crafts and knowledge of alkaline salts to Western and Southern Europe (since 7th CE)

Around 700–800 CE, the craft industry of soapmaking containing alkali plant ashes, animal fats, and the different plant oils became abundant in the Western and Southern Mediterranean, especially in Italy and Spain. This fact was mentioned in detail by Abū Mūsā Jābir ibn Ḥayyān, the Arab savant who lived in the 8th-century C.E. [40].

It should be emphasized that the English word "alkali" was "borrowed" from the Arabic language in the Middle Ages. The Arabic word القَلْوي al-qaly is the most common word for ash obtained from the alkaline saltworts plants [41]. Since ancient times, the caustic ashes' specific properties were well-known among the Middle East population. The Middle Eastern craftsmen inherited this time-honored traditional knowledge of the Ancient civilizations, whereas the Crusaders and the Arabic-speaking merchants helped disseminate this craft knowledge in Mediaeval Europe.

2.6 Declining the use of the natural alkali-bearing minerals since the industrial revolution in Europe

Until the Industrial Revolution in the 18th and 19th centuries, the caustic plant ashes had a primary use in semy-boiled body cleansing soaps possessing mild alkali pH. The natural mineral natron was the raw material for caustic washing and laundry soaps. At the end of the 18th century, Nicolas Leblanc, a French chemist, and surgeon invented an industrial process of converting the ordinary table salt, NaCl, into sodium carbonate, Na_2CO_3, to address the growing demand of the traditional industries in soda [42, 43]. Since that time, the soapmaking craft based on natural alkali-bearing minerals was gradually ousted by growing industrial technologies with chemically obtained detergents as raw materials. Industrial cleaning products of most of the 20th century have proven themselves very effective detergents. However, these artificial chemicals were found as highly allergenic and causing other unintended deleterious effects. Thus, the current trend to turn back to the traditional soapmaking crafts using the alkali-containing plant ashes has become very popular in the last years [44–46]. Thus, one more time in human history, the ancient knowledge of body cleaning and washing agents containing the plant ashes has been resurfaced and rejuvenated, being back now in human life's place.

3. Soda and potash-based glassmaking

As was previously mentioned, Leblanc's invention of artificial soda production at the end of the 18th century addressed a growing need of the European population and industry for caustic raw materials used in a) textile manufacturing as a bleaching agent; b) glassmaking as a soda-lime flux; and c) soapmaking for saponification of fats and oils [42].

3.1 2500 Year-long Ascension of crockery glassmaking based on soda and potash

Glassmaking has used natron, which is natural soda, since very ancient times. The first regularly produced glass was made in Egypt and the Near East in the sixteenth century BC [47]. The numerous archeological excavations revealed intensely colored glass, simulating precious stones such as turquoise, carnelian, lapis lazuli, amethyst, obsidian, and others, produced during the Late Bronze Age (1600–1200 BCE) [48]. Manufacturing any glass needs fluxes acting as atoms' network modifiers [49]. The network modifiers in very ancient glasses were the alkali metals and the alkali earths. The alkali metals, particularly sodium and potassium, disrupt the atom's network structure in glass, lower the melting point, and compromise the general stability of the glass (*ibid*). Alkali earths, especially calcium, usually counteract this effect to a certain extent and stabilize the glass. Ancient and historical glasses are alkali-lime-silicate glasses because alkali carbonates, such as plant ashes and natron, were the critical raw materials consciously used by glassmakers [31, 43, 48, 50–64]. It is now widely accepted that during the Late Bronze Age, Soda and potash-rich plant ash enhanced by increased lime content was the primary flux additive used to make glass in the ancient Near East [48, 50, 64, 65].

The use of natron and trona, the natural sodium carbonates, in the glassmaking of the ancient world began to be evident at *circa* 1000 BC [48] and continued almost two millennia [31, 47, 48, 53, 56, 61, 62]. The primary source of natron, for ancient Near Eastern glass manufacturing since 1600–1200 BC, was Wadi-el-Natrun, in

Egypt [31, 48, 53, 61, 62, 64, 66]. However, Pliny the Elder mentioned in his *Natural History* the natron deposits from the al-Barnuj region in the Egyptian Nile Delta, the Lake Van in the eastern region of Turkey, and the al-Jabbul lakes in Syria resources used by the ancient Greek and Roman glassmakers [67]. However, the current archeological research on the glass production in the ancient Near East in 1000 BC – 1000 AC has not provided an unambiguous opinion regarding the possibility of the ancient large-scale exploration of natron from the deposits other than Wadi-el-Natrunor al-Burnuj [54, 61]. Since the Roman era and till the 9th century BC, almost only Egyptian natron deposits supplied the flux raw material for global glassmaking. From the 7th century AC towards the end of the first millennium, the Old World's glassmaking crafts faced a shortage of mineral natron from Egypt and the Levant [51]. This natron shortage led to "re-inventing" the millennia-old alkali flux, i.e., glassmaking in Mediaeval Europe widely adopted the plant potash-ash fluxes [55, 57, 60, 63]. In the 9th and 10th centuries, the art of poly- and monochromatic luster-stained glass became very popular in the Near-Eastern Islamic world [68], see **Figure 5**.

The soda-containing flux used in Egyptian luster-stained glasses of the Islamic period (9th – 10th centuries) was natron, whereas luster-stained glass vessels from the Syria–Palestine region and Mesopotamia were crafted with sodium and potassium rich plant ashes [70].

3.2 Alkali-containing plant ashes catalyzed the invention of colored stained glass for architectural purposes

Colored stained glass has played a significant role in European architecture since the 12th century AC [60, 71, 72], see **Figure 6**.

From the 12th century up to 1440 AC, the European window glassmaking technique was a broad glass method for producing small rectangular glass sheets

Figure 5.
The ceramic dish with blue, green, and manganese-purple glaze, from Raqqa, northern Syria, 12th century AD. Presented in British museum (museum inventory number 1923.2–17.1). Picture-copyright ©discover Islamic art (MWNF) *[69].*

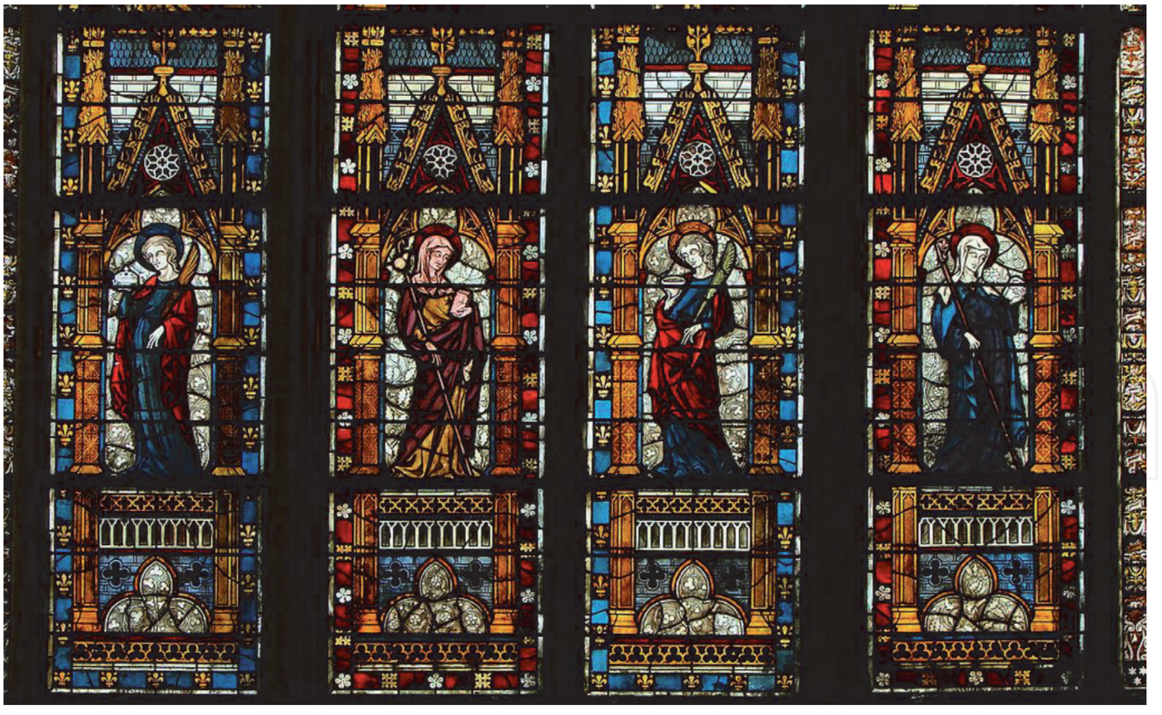


Figure 6.
A medieval window at Troyes cathedral, France (14th century). Wikipedia [73].

[43, 74]. Finally, from the 15th century until the mid-19th century, the primary window glassmaking technique in Europe was the crown glass method of producing sheet glass [74], see **Figure 7**.

Both these techniques use alkali-containing plant ashes as a flux. However, the alkali-containing plant ashes used in glassmaking differed in the different European regions. In the Eastern and Southern Mediterranean regions, the soda-rich halophytic glassworts' ash, pure or blended with natron, was imported from the Syrian-Palestine region and Egypt and widely used in glassmaking since Mediaeval times, thanks to the commercial and technological interconnections with the Islamic East [76, 77].

Since the 13th century, the glassmakers enhanced the raw plant ashes by admixture with higher lime and magnesium oxide content to obtain the glass with good chemical stability and low thermal expansion [78].

In Central Europe in the 12th – 18th centuries, the glassmaking crafts widely used potash and soda-rich wood ashes as fluxes, whereas higher contents of lead oxide and lime in ash were found effective for enhancing the glass durability [74, 79, 80].

3.3 Alkaline salts of different origins have promoted the continuous development of glass technologies for construction purposes

Towards the 15th century, window glassmaking in Central Europe began using sea salt, NaCl, as an additive to ash flux to control the window glass composition affecting glass mechanical stability [79]. As an additive to wood ash flux, sea salt, soda, and niter were widely used to produce cylinder (hull) glass, a more advanced form of broad-glass manufacture, in Central and Nothern Europe until the 17th century (see **Figures 8** and **9**). The alternative important potash-containing material used as a flux in window glass manufacturing in England till the 19th century was kelp ash [82]. Kelp ash is a substance produced by the burning of seaweed [83]. The use of kelp ash in glass manufacturing was generally declined since the first half of the 19th century because of industrial sodium carbonate manufacturing (see **Figure 8**).

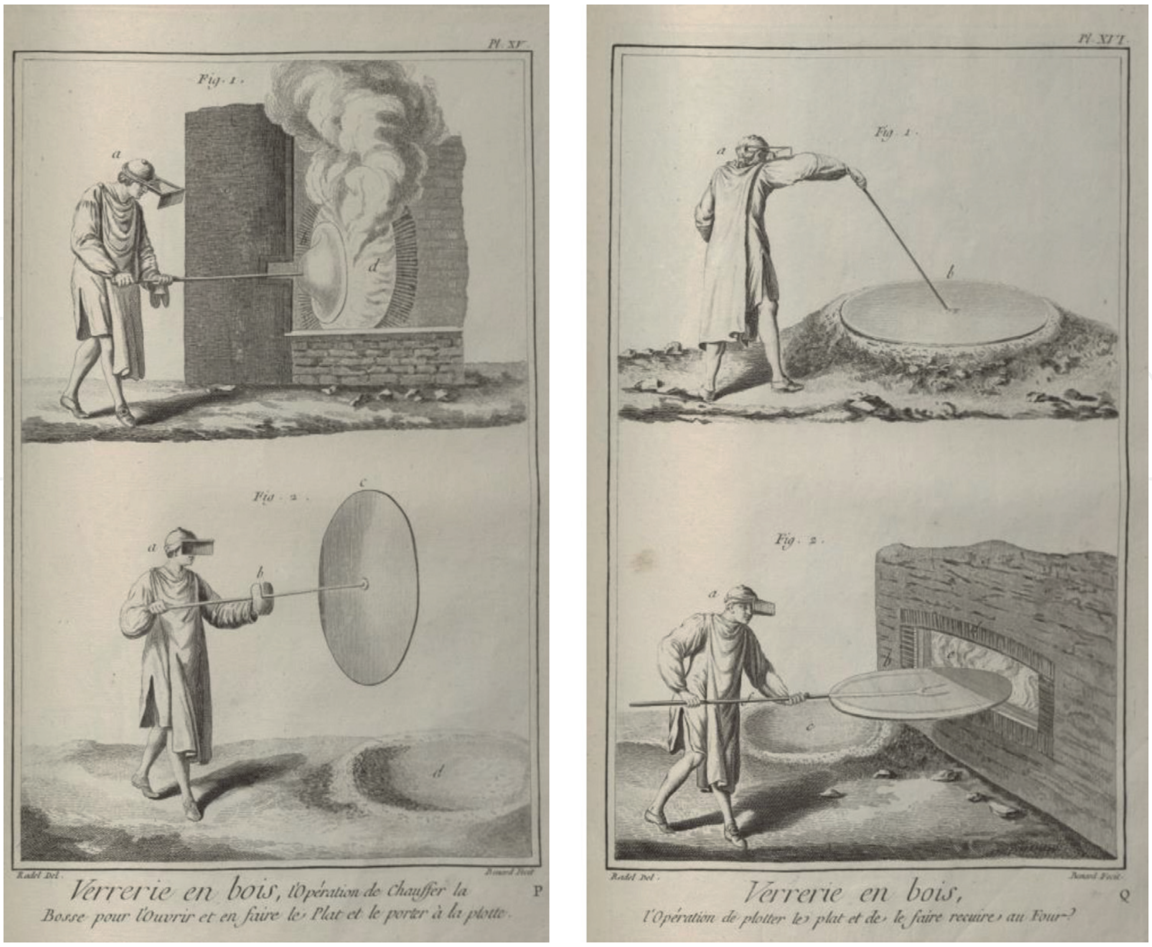


Figure 7.
*Robert Bénard (French artist, 1734–1777). Crown or window glass making engraving plates. Plates XV & XVI from [75]. The description (*in French*) of particular craft operations is also available online at [75].*

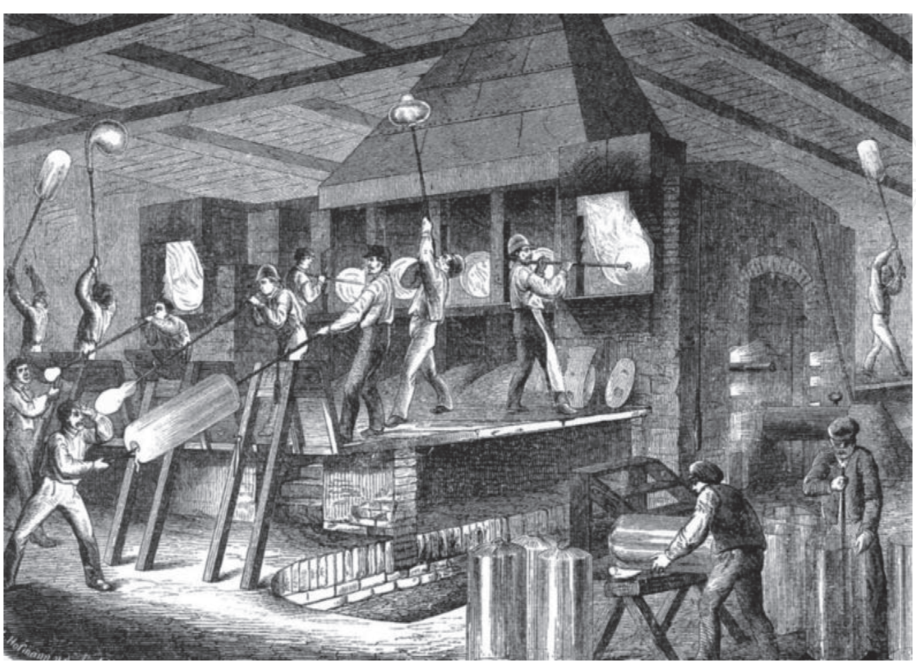
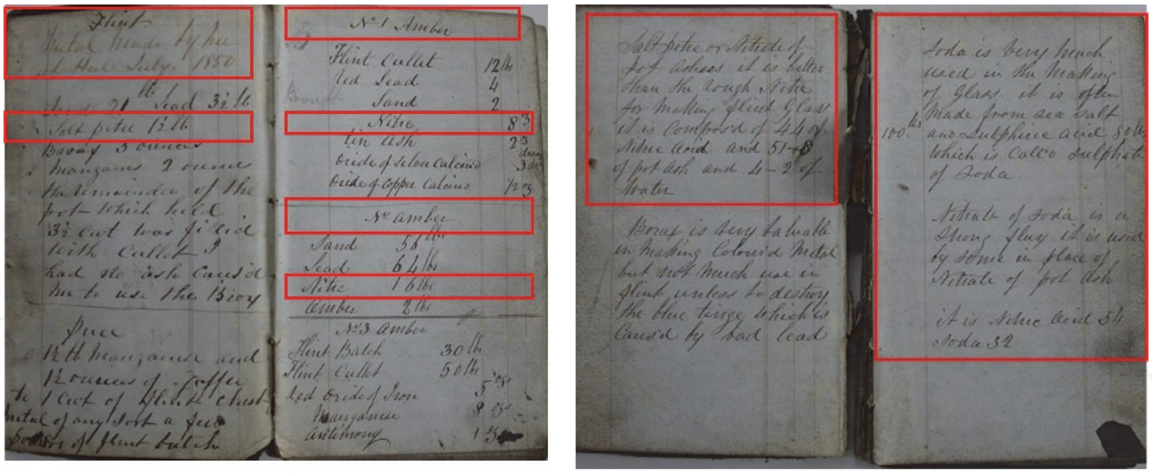


Figure 8.
Manufacturing cylinder (hull) glass. Engraving of a German glassworks, 1865. © Bildarchiv Preussischer Kulturbesitz *[81].*



a) b)

Figure 9.
1850s Original Manuscript Book of glassmaking Recipes, procedures, and Formulaes. Pictures copyright © 2021 M. Benjamin Katz, fine books/rare manuscripts (https://www.mbenjaminkatzfinebooksraremanuscripts.com/product/4340/1850s-ORIGINAL-MANUSCRIPT-BOOK-OF-GLASSMAKING-RECIPES-PROCEDURES-AND-FORMULAES-UNIDENTIFIED). a) Text in the red rectangles on the left: *"Flint. Metal made by me at Hull July 1850… Saltpeter 1½ lbs. … .".* Text in the red rectangles on the right*: "No. 1. Amber… nitre 8 oz. … . No. Amber … nitre 16 lbs". b)* Text in the red rectangles on the left: *"Saltpeter or nitrate of pot ashes it is better than the rough nitre for melting flint glass it is composed of 44% of nitric acid and 51% of pot ash and 4% of water".* Text in the red rectangles on the right*: Soda is very much used in the melting of glass it is often made from sea salt 100 lbs. and sulfuric acid 80 lbs. which is called sulphate of soda. Nitrate of soda is a strong flux it is used by some in place of nitrate of pot ash. It is nitric acid 54 soda 32."*

Using pure industrial carbonate of soda with sand and lime enabled the invention and manufacturing of a) large sheets of polished plate glass since the second half of the 19th century; b) drawn flat sheet glass from early in the 20th century; c) float glass since the late 1950s [74].

4. Conclusions

Alkali-containing salts have been the essential commodity in human life since very ancient times. Ancient civilizations studied to explore the natural resources of this commodity and developed sophisticated technological crafts and industries based on the specific properties of alkali-containing salts. For millennia this development was not based on scientific research and development but a trial-and-error approach. Nevertheless, the practical results of this empirical approach to the invention of the products based on alkali-containing salts were awe-inspiring.

Since the 19th century, synthetic alkali-containing carbonates have accelerated the industrial revolution in soap and washing detergents' production and window glass manufacturing. The invention of industrial alkali carbonate as a leading chemical commodity is fascinating because of the stages it went through; first, exploitation of natural resources for more than three and half millennia, followed by chemical industrial manufacturing for *ca.* one century, and a return to using the natural natron and plant ashes since the second half of the 20th century [84]. Turning back to the natural soda carbonate and potash resources since the late 90s of the 20th century is an obvious result of the crucial ecological approach to soap and glassmaking.

The Big History's holistic approach allows concluding that alkali-containing salts always have been essential for human well-being and highly appreciated raw materials. Thus, the millennia-old knowledge and use of this commodity have always been an authentic technological heritage.

Author details

Rina Wasserman
Department of Conservation of Sites and Monuments, Western Galilee College, Acre, Israel

*Address all correspondence to: rinaw@edu.wgalil.ac.il

References

[1] J. L. Dye, "The alkali metals: 200 years of surprises," Philos. Trans. R. Soc. A Math. Phys. Eng. Sci., vol. 373, no. 2037, p. 20140174, Mar. 2015.

[2] J. M. Thomas, P. P. Edwards, and V. L. Kuznetsov, "Sir Humphry Davy: Boundless chemist, physicist, poet and man of action," ChemPhysChem, vol. 9, no. 1, pp. 59–66, Jan. 2008.

[3] M. E. Weeks, "The discovery of the elements. IX. Three alkali metals: Potassium, sodium, and lithium," J. Chem. Educ., vol. 9, no. 6, pp. 1035–1045, Jun. 1932.

[4] The Oriental Institute and The University of Chicago, "Nippur - Sacred City Of Enlil Supreme God of Sumer and Akkad." [Online]. Available: https://oi.uchicago.edu/research/projects/nippur-sacred-city-enlil-2. [Accessed: 27-Jun-2021].

[5] M. Levey, "Ancient chemical technology in a Sumerian pharmacological tablet," J. Chem. Educ., vol. 32, no. 1, pp. 11–13, Jan. 1955.

[6] M. S. Takrouri, "Surgical, medical and anesthesia in the Middle East: Notes on Ancient and medieval practice with reference to Islamic-Arabic medicine," Internet J. Heal., vol. 5, no. 1, 2006.

[7] K. L. Konkol and S. C. Rasmussen, "An ancient cleanser: Soap production and use in antiquity," in ACS Symposium Series, vol. 1211, 2015, pp. 245–266.

[8] J. A. Halloran, Sumerian Lexicon. A Dictionary Guide to the Ancient Sumerian Language. Logogram Publishing, 2006.

[9] E. Peter, Sumerian Cuneiform English Dictionary. CreateSpace Independent Publishing Platform, 2014.

[10] Museum of Anthropology and Archaeology: Babylonian Section., "Pennsylvania Sumerian Dictionary," University of Pennsylvania, 2006. [Online]. Available: http://psd.museum.upenn.edu/. [Accessed: 27-Jun-2021].

[11] M. S. Tite, A. Shortland, Y. Maniatis, D. Kavoussanaki, and S. A. Harris, "The composition of the soda-rich and mixed alkali plant ashes used in the production of glass," J. Archaeol. Sci., vol. 33, no. 9, pp. 1284–1292, Sep. 2006.

[12] S. T. Ahmad, N. A. K. K. Sima, and H. H. Mirzaei, "Effects of sodium chloride on physiological aspects of salicornia persica growth," J. Plant Nutr., vol. 36, no. 3, pp. 401–414, Mar. 2013.

[13] D. Loconsole, G. Cristiano, and B. De Lucia, "Glassworts: From wild salt marsh species to sustainable edible crops," Agric., vol. 9, no. 1, p. 14, Jan. 2019.

[14] M. Levey, "The early history of detergent substances: A chapter in Babylonian chemistry," J. Chem. Educ., vol. 31, no. 10, pp. 521–524, Oct. 1954.

[15] Glosbe - The biggest online dictionary, "English-Akkadian dictionary." [Online]. Available: https://en.glosbe.com/en/akk/salt. [Accessed: 27-Jun-2021].

[16] J. Black, A. George, and N. Postgaye, Eds., A Concise Dictionary of Akkadian, 2nd (corre. Wiesbaden: Harrassowitz Verlag, 2000.

[17] D. Potts, "On Salt And Salt Gathering In Ancient Mesopotamia," J. Econ. Soc. Hist. Orient, vol. 27, no. 3, pp. 225–271, 1984.

[18] M. Levey, "Gypsum, Salt and Soda in Ancient Mesopotamian Chemical Technology," Isis, vol. 49, no. 3, pp. 336–342, Sep. 1958.

[19] J. A. E. Nenquin, "Salt. A Study in Economic Prehistory. Dissertationes Archaeologicae Gandenses, 6," De Tempel, vol. 6, 1961.

[20] J. Lines and D. J. Wiseman, The Alalakh Tablets, vol. 59, no. 4. London: British Institute of Archaeology at Ankara, 1955.

[21] FDA - U.S. Food and Drug Administration, "Sodium in Your Diet," 15/09/2020, 2012. [Online]. Available: https://www.fda.gov/food/nutrition-education-resources-materials/sodium-your-diet#:~:text=Americans eat on average about,about 1 teaspoon of salt! [Accessed: 05-Feb-2021].

[22] Joint Research Centre - European Commission, "Health promotion and disease prevention Knowledge Gateway - Whole Grain," Postgraduate Medicine, 2017. [Online]. Available: https://ec.europa.eu/jrc/en/health-knowledge-gateway/promotion-prevention/nutrition/whole-grain. [Accessed: 05-Feb-2021].

[23] J. R. Partington, A History of Greek Fire and Gunpowder. Baltimore, Mariland, USA: JHU Press, 1998.

[24] D. Cressy, Saltpeter: The Mother of Gunpowder. Oxford, UK: Oxford University Press, 2013.

[25] M. Maurer, P. Schwegler, and T. A. Larsen, "Nutrients in urine: Energetic aspects of removal and recovery," Water Sci. Technol., vol. 48, no. 1, pp. 37–46, Jul. 2003.

[26] M. Maurer, W. Pronk, and T. A. Larsen, "Treatment processes for source-separated urine," Water Res., vol. 40, no. 17, pp. 3151–3166, Oct. 2006.

[27] Z. Ganrot, G. Dave, and E. Nilsson, "Recovery of N and P from human urine by freezing, struvite precipitation and adsorption to zeolite and active carbon," Bioresour. Technol., vol. 98, no. 16, pp. 3112–3121, Nov. 2007.

[28] K. M. Udert and M. Wächter, "Complete nutrient recovery from source-separated urine by nitrification and distillation," Water Res., vol. 46, no. 2, pp. 453–464, Feb. 2012.

[29] C. M. Mehta, W. O. Khunjar, V. Nguyen, S. Tait, and D. J. Batstone, "Technologies to recover nutrients from waste streams: A critical review," Crit. Rev. Environ. Sci. Technol., vol. 45, no. 4, pp. 385–427, Feb. 2015.

[30] T. M. L, "Egyptian soda," Nature, vol. 90, no. 2254, pp. 527–528, Jan. 1913.

[31] Melanie Sapsford, "The use of sodium salt deposits in medical and medically associated industries in Ancient Egypt.," Cranfield University, 2009.

[32] A.-M. Gomaa and A. Elamin, "A review on the materials used during mummification processes in Ancient Egypt," Mediterr. Archaeol. Archaeom., vol. 11, no. 2, pp. 129–150, 2011.

[33] A. S. Zaky et al., "Mid-to Late Holocene paleoclimatic changes and paleoenvironmental shifts inferred from pollen and diatom assemblages at Lake Hamra, Wadi El Natrun (Western Nile Delta, North Western Desert, Egypt)," Quat. Int., vol. 542, pp. 109–120, Mar. 2020.

[34] P. J. Moorad, "A comparative study of medicine among the Ancient races of the East: Egypt, Babylonia and Assyria," Ann. Med. Hist., vol. 9, pp. 155–167, 1937.

[35] B. Davis and J. Toivari, "A Letter of Reproach (O. DeM 314). Corruption in the Administration of the Washing Service at Deir El-Medina," in Deir El-Medina in the Third Millennium AD. A Tribute to Jac. J. Janssen, R. J. Demaree and A. Egberts, Eds. 2000, pp. 65–77.

[36] S. Isserow and H. Zahnd, “Chemical knowledge in the old testament,” J. Chem. Educ., vol. 20, no. 7, pp. 327–335, Jul. 1943.

[37] H. B. Routh, K. R. Bhowmik, L. C. Parish, and J. A. Witkowski, “Soaps: From the phoenicians to the 20th century—A historical review,” Clin. Dermatol., vol. 14, no. 1, pp. 3–6, Jan. 1996.

[38] K. L. Konkol and S. C. Rasmussen, “An Ancient Cleanser: Soap Production and Use in Antiquity,” 2015, pp. 245–266.

[39] N. Everett, The Alphabet of Galen: Pharmacy from Antiquity to the Middle Ages: Pharmacy from Antiquity to the Middle Ages: A Critical Edition of the Latin Text Paperback. Toronto, Canada: University of Toronto Press, 2012.

[40] A. S. . Davidsohn, “Soap and detergent,” Encyclopedia Britannica, 2020. [Online]. Available: https://www.britannica.com/science/soap. [Accessed: 23-Mar-2021].

[41] M. Levey, “Mediaeval Arabic Bookmaking and Its Relation to Early Chemistry and Pharmacology,” Trans. Am. Philos. Soc. New Ser., vol. 52, no. 4, pp. 1–79, 1962.

[42] M. Cook, “The Leblanc Soda Process. A Gothic Tale for Freshman Engineers,” Chem. Eng. Educ., vol. 32, no. 2, pp. 133–137, 1998.

[43] D. Dungworth, “The Value of Historic Window Glass,” Hist. Environ. Policy Pract., vol. 2, no. 1, pp. 21–48, Jun. 2011.

[44] H. O. Ogunsui and C. A. Akkinawo, “Quality Assessment of Soaps Produced from Palm Bunch Ash-Derived Alkali and Coconut Oil,” J. Appl. Sci. Environ. Manag., vol. 16, no. 4, pp. 363–366, 2012.

[45] M. D. Torres and J. Seijo, “By-Products from the Chestnut Industry Used to Produce Natural Potassium Soaps: Physicochemical Properties,” J. Surfactants Deterg., vol. 19, no. 2, pp. 381–387, Mar. 2016.

[46] O. Atolani et al., “Green synthesis and characterisation of natural antiseptic soaps from the oils of underutilised tropical seed,” Sustain. Chem. Pharm., vol. 4, pp. 32–39, Dec. 2016.

[47] A. J. Shortland and T. Rehren, “Glass,” in Archaeological Science, M. P. Richards and K. Briton, Eds. Cambridge University Press, 2020, pp. 347–364.

[48] T. Rehren and D. Rosenow, “Three Millennia of Egyptian Glassmaking,” in Mobile Technologies in the Ancient Sahara and Beyond, Cambridge University Press, 2020, pp. 423–450.

[49] J. E. Shelby, Introduction to Glass Science and Technology, 3rd Editio. Cambridge: Royal Society of Chemistry, 2020.

[50] A. E. Marshall, “An Assyrian text on glass manufacture,” J. Chem. Educ., vol. 10, no. 5, p. 267, May 1933.

[51] C. M. Jackson, S. Paynter, M.-D. Nenna, and P. Degryse, “Glassmaking using natron from el-Barnugi (Egypt); Pliny and the Roman glass industry,” Archaeol. Anthropol. Sci., vol. 10, no. 5, pp. 1179–1191, Aug. 2018.

[52] C. M. Jackson, C. A. Booth, and J. W. Smedley, “Glass by Design? Raw Materials, Receipes and Compositional Data,” Archaeometry, vol. 47, no. 4, pp. 781–795, Nov. 2005.

[53] J. Hemderson, “The Raw Materials of Early Glass Production,” Oxford J. Archaeol., vol. 4, no. 3, pp. 267–291, Nov. 1985.

[54] G. Dardeniz, “Was Ancient Egypt the Only Supplier of Natron? New Research Reveals Major Anatolian

Deposits," in Anatolica XLI (Volume 41), 2015, pp. 191–202.

[55] Z. Cílová and J. Woitsch, "Potash – a key raw material of glass batch for Bohemian glasses from 14th–17th centuries?," J. Archaeol. Sci., vol. 39, no. 2, pp. 371–380, Feb. 2012.

[56] G. H. Barfod, I. C. Freestone, A. Lichtenberger, *R. Raja*, and H. Schwarzer, "Geochemistry of Byzantine and Early Islamic glass from Jerash, Jordan: Typology, recycling, and provenance," Geoarchaeology, vol. 33, no. 6, pp. 623–640, Nov. 2018.

[57] A. B. Babalola, L. Dussubieux, S. K. McIntosh, and T. Rehren, "Chemical analysis of glass beads from Igbo Olokun, Ile-Ife (SW Nigeria): New light on raw materials, production, and interregional interactions," J. Archaeol. Sci., vol. 90, pp. 92–105, Feb. 2018.

[58] M. S. Tite, A. Shortland, Y. Maniatis, D. Kavoussanaki, and S. A. Harris, "The composition of the soda-rich and mixed alkali plant ashes used in the production of glass," J. Archaeol. Sci., vol. 33, no. 9, pp. 1284–1292, Sep. 2006.

[59] W. B. Stern and Y. Gerber, "Potassium-Calcium Glass: New Data and Experiments*," Archaeometry, vol. 46, no. 1, pp. 137–156, Feb. 2004.

[60] J. Smedley, C. M. Jackson, and C. A. Booth, "Back to the Roots: the Raw Materials, Glass Receipes and Glassmaking Practices of Theophilus.," in The Prehistory and History of Glassmaking Technology, Westerville, Ohio: The American Ceramic Society, 1998, pp. 145–165.

[61] A. Shortland, L. Schachner, I. Freestone, and M. Tite, "Natron as a flux in the early vitreous materials industry: sources, beginnings and reasons for decline," J. Archaeol. Sci., vol. 33, no. 4, pp. 521–530, Apr. 2006.

[62] A. J. Shortland, P. Degryse, M. Walton, M. Geer, V. Lauwers, and L. Salou, "The Evaporitic Deposits of Lake Fazda (Wadi Natrun, Egypt) and Their Use in Roman Glass Production," Archaeometry, vol. 53, no. 5, pp. 916–929, Oct. 2011.

[63] T. Rehren and M. Brüggler, "The Late Antique glass furnaces in the Hambach Forest were working glass - not making it," J. Archaeol. Sci. Reports, vol. 29, p. 102072, Feb. 2020.

[64] T. Rehren, "A review of factors affecting the composition of early Egyptian glasses and faience: alkali and alkali earth oxides," J. Archaeol. Sci., vol. 35, no. 5, pp. 1345–1354, May 2008.

[65] K. Kanungo and R. H. Brill, "Kopia, India's First Glassmaking Site: Dating and Chemical Analysis," J. Glass Stud., vol. 51, pp. 11–25, 2009.

[66] P. Degryse, R. B. Scott, and D. Brems, "The archaeometry of ancient glassmaking: reconstructing ancient technology and the trade of raw materials," Perspective, no. 2, pp. 224–238, Dec. 2014.

[67] Pliny, Natural History, vol. 8. Cambridge, Mass. and London: Loeb Classical Library, 330, 1963.

[68] Y. Shindo, "Islamic Lustre-Stained Glass from Raya between the Ninth and Tenth Centuries," in AIHV du 16e Congrès. London 2003, 2005, pp. 174–177.

[69] E. Shovelton, "Ceramic dish," Discover Islamic Art, Museum With No Frontiers, 2021. [Online]. Available: http://islamicart.museumwnf.org/database_item.php?id=object;ISL;uk;Mus01;14;en&cp. [Accessed: 29-Jun-2021].

[70] N. Kato, I. Nakai, and Y. Shindo, "Transitions in Islamic plant-ash glass vessels: on-site chemical analyses conducted at the Raya/al-Tur area on

the Sinai Peninsula in Egypt," J. Archaeol. Sci., vol. 37, no. 7, pp. 1381–1395, Jul. 2010.

[71] R. W. Sowers, "Stained glass," Encyclopedia Britannica. 2021.

[72] H. Louw, "The Development of the Window," in Windows, Routledge, 2015, pp. 7–96.

[73] Wikipedia – the Free Encyclopedia, "Medieval stained glass" [Online]. Available: https://en.wikipedia.org/wiki/Medieval_stained_glass. [Accessed: 27-Jule-2021].

[74] Historic England, "Traditional Windows: Their Care, Repair and Upgrading," p. 74, 2014.

[75] "Verrerie . Verrerie en Bois, ou Grande Verrerie a Vitres ou en Plats. Eds. Denis Diderot and Jean le Rond D'Alembert. Paris: Chez Briasson, David & Le Breton-1767," University of Chicago: ARTFL Encyclopédie Project. University of Chicago. [Online]. Available: https://artflsrv03.uchicago.edu/philologic4/encyclopedie1117/navigate/27/31/. [Accessed: 29-June-2021]

[76] A. Silvestri and A. Marcante, "The glass of Nogara (Verona): a 'window' on production technology of mid-Medieval times in Northern Italy," J. Archaeol. Sci., vol. 38, no. 10, pp. 2509–2522, Oct. 2011.

[77] S. Cagno, L. Favaretto, M. Mendera, A. Izmer, F. Vanhaecke, and K. Janssens, "Evidence of early medieval soda ash glass in the archaeological site of San Genesio (Tuscany)," J. Archaeol. Sci., vol. 39, no. 5, pp. 1540–1552, May 2012.

[78] S. C. Rasmussen, "Advances in 13th Century Glass Manufacturing and Their Effect on Chemical Progress," Bull. Hist. Chem., vol. 33, no. 1, pp. 28–33, 2008.

[79] O. Schalm, K. Janssens, H. Wouters, and D. Caluwé, "Composition of 12–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings," Spectrochim. Acta Part B At. Spectrosc., vol. 62, no. 6–7, pp. 663–668, Jul. 2007.

[80] K. Janssens, S. Cagno, I. De Raedt, and P. Degryse, "Transfer of Glass Manufacturing Technology in the Sixteenth and Seventeenth Centuries from Southern to Northern Europe: Using Trace Element Patterns to Reveal the Spread from Venice via Antwerp to London," in Modern Methods for Analysing Archaeological and Historical Glass, K. Janssens, Ed. Oxford, UK: John Wiley & Sons Ltd, 2013, pp. 537–562.

[81] Encyclopædia Britannica, "The making of broad glass, from an engraving of a German glassworks, 1865," Encyclopædia Britannica. [Online]. Available: https://www.britannica.com/topic/glass-properties-composition-and-industrial-production-234890/History-of-glassmaking#/media/1/234890/261. [Accessed: 29-June-2021].

[82] *W. Cooper*, The crown glass cutter and glazier's manual. Edinburgh: Oliver & Boyd, 1835.

[83] The Editors of Encylopedia, "Kelp," Encyclopedia Britannica, 2020. [Online]. Available: https://www.britannica.com/science/kelp. [Accessed: 06-Apr-2021].

[84] J. Wisniak, "Sodium carbonate — From natural resources to Leblanc and back," Indian J. Chem. Technol., vol. 10, no. 1, pp. 99–112, 2003.