FRANCIS HOME AND JOSEPH BLACK: THE CHEMISTRY AND TESTING OF ALKALINE SALTS IN THE EARLY BLEACHING AND ALKALI TRADE

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This paper considers the analytical work of two chemists in Scotland during the second half of the 18th century. It examines their efforts to understand and determine the strength of alkaline salts at a time when quantitative analytical measurement was beginning to be made in a form recognizable by present day chemists. In this period atomic weights and chemical formulae, which we now regard as essential aids in analysis, had not come into being. There is therefore a temptation for present day chemists to regard the period as one in which quantitative chemical analysis seemed almost impossible. It will be shown however that the analytical methods and chemical thinking of Francis Home (1719-1813) and Joseph Black (1728-1799) were adequate for the needs of the early alkali trade and the use of these alkaline materials in bleaching.

The Chemical Revolution of Archibald Clow and Nan Clow is of particular value to historians for its account of the early Scottish kelp industry as a source of natural alkali (1). These authors made little reference to analytical chemistry associated with this industry, although Tennant's method of estimating barilla (impure alkali) was given as an example of volumetric analysis (2). A full critical review of this book was made by F. W. Gibbs, who confirmed the Clows' view that the growth of 18th-century chemistry was paralleled by a corresponding growth of chemical manufacturing (3).

The early bleaching industry depended upon the cleansing properties of alkali solutions, and before the synthetic alkali of Leblanc became available the industry used natural alkali from kelp and other plant origins. Since chemical analysis was regarded as of limited value to the manufacture of Leblanc alkali (4), it is not surprising that earlier analytical requirements remained of secondary importance.

The Early Bleaching Industry in Scotland

The empirically based art of bleaching had origins in Hellenistic technology but by what route the methods became common in Britain is uncertain (5). The Netherlands and Germany appear to have been the first in Europe in this field (6), and it was to these countries that Britain sent linen from its expanding textile industry to be bleached and then returned, thus establishing a seasonal export-import business. Such trade, known to have occurred within the first few decades of the 1700s, diminished when satisfactory bleaching operations were established in Britain; but the process remained slow and complicated. For example, a typical "bucking" (alkaline wash) solution might be made thus (7):

> *The Concentrate*: Blue ashes (30 lb); White pearl ashes (30 lb); Marcoft ashes (200 lb) or Cashub ashes (300 lb); and Muscovy ashes (300 lb) placed in water to make up to 170 gallons.
> *Bucking Liquid:* 2 gallons of the above slurry were combined with 2 lb of soap, and the whole was then made up to 40 gallons.

The linen would be steeped in this kind of alkaline solution for some hours, followed by several washes in water and repeated buckings, finally being "soured" in buttermilk residues (lactic acid), washed and exposed to sunlight until some satisfactory degree of bleaching had been achieved.

This was a typical bleaching operation at the time Home and Black were considering the topic. Clearly, a cursory glance at the bucking solution formula above, with its puzzling admixture of similar materials, suggests it was the outcome of an empirically based development. These empirical activities lacked chemical understanding we now have. It was Dr. Francis Home who changed this situation, and his influence was recognized in an early history of this industry by Higgins (8). In 1952 Clow and Clow considered the importance of Joseph Black's analysis of various kelps but gave no description of any contemporary chemical methods (9). There is a similar absence of practical analytical procedure in the work by Musson and Robinson although they clearly showed the work of Home and Black in the wider context of the association of science with industry (10).

Francis Home, courtesy of the Wellcome Trust

Home suggested the use of sulfuric acid instead of milk sours, and this may have been one reason why John Roebuck (1718-1794) and Samuel Garbett (1717-1807) set up their acid works at Prestonpans near Edinburgh in 1749 (11). Whether Roebuck foresaw the potential market in this new industry is not known; but according to Jardine (1796) (12), several of Roebuck's chemical friends knew that he (Roebuck) had tried out the "bleaching" effect of sulfuric acid even before the publication of Home's *Experiments on Bleaching* in 1756. Durie (13) has suggested that it was Roebuck's partner, Samuel Garbett, who initiated early tests with acid. The availability and low cost of acid from the Prestonpans works may have stimulated interest in the use of that product in the bleaching process.

Francis Home and Joseph Black

Home's publication of 1756, *Experiments on Bleaching* (7), was followed by a second Dublin edition in 1771 (14). In this second edition there is an appendix written by Black (Fig. 1 and 2) entitled "An Explanation of the Effect of Lime upon Alkaline Salts: and a Method pointed out whereby it may be used with Safety and Advantage in Bleaching" (15). Also included are "An Experimental Essay on the Use of Leys and Sours in Bleaching" by James Ferguson (16), and "An Abstract of the foregoing Essays, containing, Practical Rules and Plain Directions for the Preparation and Use of the Sours made of Oil of Vitriol, and of the Leys made of Bleaching-ashes with the addition of Quicklime." The title page (opposite page 282) names David Macbride as author.

In 1768 Francis Home became the first Professor of Materia Medica at the University of Edinburgh (17). He had been born almost 50 years earlier at Eccles in Berwickshire and after taking his M.D., at Edinburgh in 1750, he practiced in that city. His professorship (1768-1798) was contemporaneous with that of Joseph Black's (1766-1799), and both were Fellows of the Royal College of Physicians for 30 years; clearly, they knew each other well.

At that time the scale of bleaching operations was expanding and efforts were being made to improve the treatment of cotton and linen, particularly in the final stages of finishing. If this expansion were to continue, then a faster and more efficient method of bleaching would be necessary. The time saved by using sulfuric acid was its main advantage and this accounts for its use by the industry. It can be argued that the innovations involving the use of chemicals in bleaching during the 18th century arose, not from rising costs caused by the uncertain availability of raw materials and shortage of land for bleach fields, but by the slowness of the field bleaching method itself (18). The Board of Trustees for Fisheries, Manufactures and Improvements in Scotland (hereafter referred to as the Board of Trustees) concerned itself with the protection of the quality of manufactured cloth and in particular with the nature of prevailing bleaching processes. To this end Francis Home was invited to provide a course of lectures on the subject, and by these means his recommendation to use sulfuric acid instead of milk sours became known. The use of acid (19):

> ..will answer to all the purposes of milk and bran sours; nay, in several respects, be much preferable to them. I am of the opinion that five hours will do as much with this sour, as five days with the common sort.

His suggestion, slow to gain interest initially, was by the 1770s ultimately adopted in the Scottish bleach fields and was supported by the Board of Trustees, who in 1756 had awarded a premium of £100 to Home "for ingenious and useful experiments in the Art of Bleaching" (20). At that time sulfuric acid was becoming more readily available from the new lead chamber method of manufacture. In the same year (1756) William Cullen (1710-1790) was appointed Professor of Chemistry at Glasgow University after having submitted to the Board of Trustees his experimental results regarding chemical aspects of the bleaching industry and the use of timber and sea weed as sources of ashes (21).

It seems reasonable to suppose that alkaline bucking solutions were used in the bleaching process because of their cleansing and detergent value (22). The use of soda in some form has for these reasons been retained to this day. Nevertheless it is difficult to account for the apparent complexity of these early alkaline washes (their composition is discussed later). Of course, empirically influenced adjustments would be made from time to time, and the reasons for these would no doubt have become obscure with the passage of time. At some time in the past, lime was included in these formulations and found to give a better result; but because lime was known to degrade linen fibers, government control interceded to protect the standard of workmanship. Indeed, "the use of lime in bleaching was forbidden by law, although Francis Home in 1756 said it was used in Manchester and in Scotland" (23). Clearly there were divergent opinions and misunderstandings about the use of lime; with this background and in the knowledge of its prohibition Home applied his chemical knowledge to improve the bleaching process. His realization of the scant understanding within the industry, and perhaps also government, probably motivated his researches. Working without the advantages given by chemical formulae, he analyzed materials used in bucking solutions, particularly the expensively imported Muscovy ashes, and showed that these were significantly different from others such as common pearl ashes and blue ashes.

Steeped in modern terminology, we may no longer have the ability to appreciate a reaction without benefit of composition and a balanced chemical equation. This however, can be misleading since our modern language of chemistry incorporates the solutions to the very problems that so troubled the 18th-century chemists. Nevertheless, it will be shown that Black's study of the decomposition of magnesium and calcium carbonates played an important part in chemical enlightenment, particularly in Scotland, and this, together with Home's work, influenced chemical understanding and analysis concerned with bleaching.

In the absence of archival evidence it is difficult to assess with any certainty the personal familiarity and communication between Francis Home and Joseph Black. One important biographer of Black, Sir William Ramsay, listed Black's colleagues and friends but made no mention of Francis Home (24). It seems inconceivable that there was no regular communication between them in view of their parallel academic positions (25). However, the results of their individual chemical researches overlapped and reinforced each other to the advantage of established bleaching processes. Black's chemical theory reinforced Home's practical contribution as seen in the 1771 edition of *Experiments on Bleaching*, and it is important to note that their work opened the way and encouraged further analytical progress.

Home's *Experiments on Bleaching* 1771

From this second edition we find that:

1. Home, analyzed various alkaline salts including pearl ashes and blue ashes (26):

> In order to discover what effect acids would have on these ashes, and what quantity of the former the latter would destroy; from which I might be able to form some judgement of the quantity and strength of the salt they contained; I took a drachm [*one-sixteenth of an ounce, assuming Avoirdupois*] of blue pearl ashes, and poured on it a mixture of one part spirit of nitre, and six parts water; which I shall always after-

> wards use, and call the *acid mixture*. An effervescence arose, and, before it was finished, 12 tea-spoonfuls of the mixture were required. This effervescence with each spoonful of the acid mixture was violent, but did not last long.

This was Home's method of measuring the strength of the alkali salt by neutralizing a weighed amount with a measured quantity of acid of known strength. He warned however that this measurement is not the entire truth "...as there are other bodies beside alkaline salts, that effervesce with acids" (27). In a later experiment the importance of purity was shown and the process of crystallization was described (28).

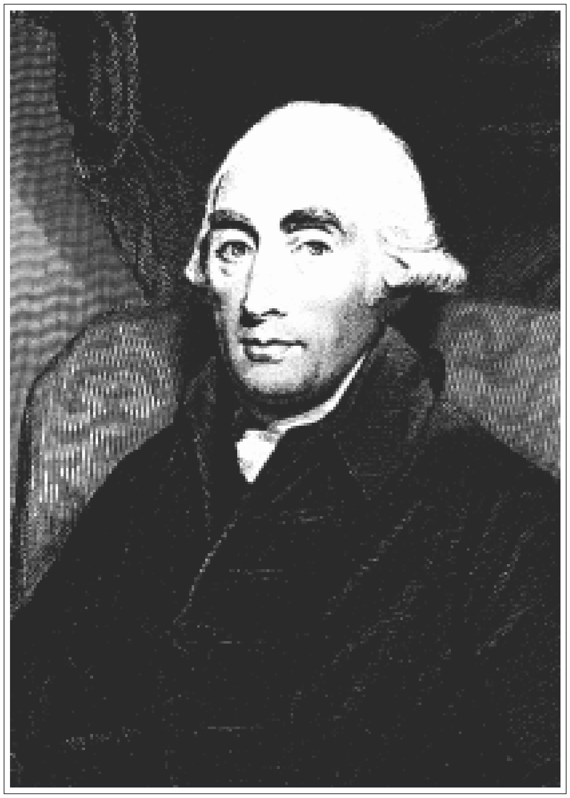
2. In experiment number 27 he showed Muscovy ashes to be different from pearl ashes and blue ashes in that the more expensive imported material contained an alkaline salt (potassium hydroxide) and lime, "and the latter in much greater proportion than the former" (29).

3. Having developed a method of testing alkaline salts that bleachers could carry out for themselves, he constantly recommended experimentation as the best means to improve bleaching operations.

4. He emphasized that it was unnecessary to buy Muscovy ashes, as the same result could be achieved by mixing pearl ashes with quicklime (CaO).

5. He showed that lime degrades cloth but, if mixed with ordinary pearl ashes or blue ashes, the bleaching action (cleansing) was accelerated without damage to the cloth. This he proved by trials in the bleach fields.

6. He confirmed that Muscovy ashes on their own gave good whiteness but some degradation of the cloth fibers. Home then established the reasons for the composition of bucking solutions and the use of Muscovy ashes, provided they were mixed with a certain amount of pearl ash or blue ash. In this he showed the importance and value of chemists and of chemical knowledge in bringing about technical improvements in industrial processes.



Joseph Black (1728-1799)

Although early bleachers had learned, by their trial and error methods, the value of including Muscovy ashes in their bucking solutions, they were unaware, prior to Home's work, that this arose from the lime content, and that addition of lime itself to blue ashes and pearl ashes therefore provided a much cheaper means of achieving the same result. Home found the explanation in terms of chemistry and analysis although, according to Edelstein (30), he employed empirical means in determining the optimum ratio of alkaline salts (blue and pearl ashes) to added lime. He certainly had a good empirical appreciation of the practical value of the admixture of ashes with lime in bucking solutions whereby mild alkali was converted to caustic alkali, while the lime was precipitated as chalk. He appears however to have had only limited theoretical insight into the underlying chemistry. What he did not understand, however, and what Black added, was the exact interpretation of this reaction, as involving the transfer of fixed air.

Joseph Black's Contribution

Black had established the chemical nature of lime and fixed air (carbon dioxide) through his now well known work on magnesia alba (magnesium carbonate) and quicklime, which involved accurate quantitative analysis. His experiments showed that caustic alkalis were merely alkali salts deprived of their carbon dioxide or fixed air (31):

> ..the lime is found to have attracted and detained a considerable part of the salts of the ley, or more properly to have attracted and detained a substance which before was attached to the salts.

It was this new insight which, while adding greatly to the current chemical knowledge, was also relevant to the bleaching industry.

Limestone had for many centuries provided lime, and it seems natural that the early bleaching artisans should see this material as a possible helpful additive to their process. Modern elementary chemistry shows that by "burning" limestone and dissolving the quicklime in water, lime water (a saturated solution of calcium hydroxide) is formed. Slaked lime (calcium hydroxide), being only slightly soluble, persisted as undissolved, suspended solid in bleachers' solutions. It was this material that was so detrimental to the cloth and caused yellowing and fiber degradation. For these reasons the use of lime in bleaching was forbidden by law (32). This legislation was proved to be in error by Home and Black although confusion and misunderstanding of the processes continued, even into recent biographical accounts (33). Limewater in itself had no harmful effect but undissolved slaked lime did. However, this latter constituent would have been absent so long as an excess of ashes remained (34). Black showed that the reaction of limewater, or undissolved slaked lime (calcium hydroxide) with ashes, i.e., causticization, removed the potentially harmful lime, producing very desirable strong caustic and innocuous chalk (calcium carbonate).

Furthermore, Black noted (35):

> ..that if we free the bleaching salts entirely of this air [the carbon dioxide], they will be so much the more active and powerful, and that a smaller quantity of them will serve the purpose, than when used in their present state.

Appreciating the technical advantage of the expensive Russian imported ashes, in that "the whole, or very near the whole of the air [carbon dioxide] has been separated already" (36), Black made the case for using lime with the much cheaper ashes made from kelp, in order to achieve a similar degree of bleaching. There were clear hints here about the value of quality control and the purity of the lime and nature of the ashes. More importantly perhaps for future chemistry, he noted explicitly "that lime and Mephitic air [carbon dioxide] are capable of uniting together in one certain proportion only" (37). He described a simple observation to determine the required amount of lime but added (38):

> ..a bleacher however, who generally uses the same kind of lime and the same kind of ashes, will soon learn by the help of these trials to hit the due proportion so nearly as to need no amendment.

Conclusions

With Black's theory and Home's *Experiments on Bleaching*, the ill-founded laws forbidding the use of lime could be questioned. Whatever reasons had initiated this legislation, it was the work of Home and Black that showed it to be unnecessary. Black in particular had provided chemical principles that found application in bleaching; he brought a new chemical understanding, made available through laboratory based chemical experiment and analysis.

Of course, sunlight continued to play an important part in the bleaching process and some seasonal limitations continued. The increasing use of sulfuric acid instead of milk sours sped up the process whereby mineral deposits on the cloth were removed, which otherwise might act as mordants at a later stage of dyeing. Nevertheless the process remained slow and cumbersome. Fears of the consequences of mistakes when using this acid lingered despite the fact that Home had shown its safe use by experiment (39). A Manchester physician, Dr A. Eason, having industrial chemical interests, advocated the use of muriatic acid (hydrochloric) instead of vitriol, but there is little evidence the former gained common use in the industry (40).

Black's correspondence with James Ferguson of Belfast, another contributor to the *Appendix* in the 1771 Dublin edition of Home's *Experiments on Bleaching*, is seen in Ramsey's (1918) biography of Black as documentary evidence of Black's involvement in the bleaching industry (41). Indeed, the wording in these letters closely resembles that used by Black in the *Appendix*. It is to Ferguson, according to Edelstein (42), that credit should be given for promoting the work of both Black and Home, whose chemical and analytical work no doubt influenced the relaxation and later repeals of the existing laws regarding the use of lime (43). Black reported in his paper that by chemical analysis and practical testing, those ashes containing "a salt that is most free from the above-mentioned aerial matter" [fixed air], can be shown to be the most effective (44). This was shown by the analysis and use of Muscovy ashes, which contained free or caustic alkali. Black argued that there was no reason for distrusting and avoiding lime in bleaching if it was used in the presence of excess ashes. The process of causticization was not new but Black was the first to provide its chemical understanding.

It is not certain what motivated Black and Home in their work related to the bleaching industry. We know that their chemical achievements occurred in a period now described as the Scottish Enlightenment, when anticipations concerning the usefulness of chemistry were running high and were reinforced by accumulated knowledge (45). It seems reasonable that Black and Home, if motivated by this growth of chemical knowledge, would seek to establish its practical application in the already expanding industrial processes.

The Board of Trustees saw the need for a low-cost alkali without the restraints of imported material. Thus, the opportunity for chemistry and the application of scientific knowledge became apparent and a part, albeit small, of the early industrial revolution in Britain.

The role of chemical analysis at that time was not clearly defined or obvious, and those active in this practice were singularly few when one considers the growing interest in chemistry. Furthermore, where analytical results were obtained, could these have been realistically employed by early chemical plant artisans? Bleaching processes were already established when legal intervention (perhaps based on ill-judged chemistry) prohibited the use of cheap lime, but it was chemistry that influenced its future repeal. The analytical chemistry of Home and Black was unlikely to have been seen as an immediate impetus to greater production in the textile industry. However, their work provided the theoretical basis on which the processes and materials used in the industry could be understood and measured. The relatively simple observation by Home that sulfuric acid allowed rapid bleaching probably affected the overall industry more than any advantages gained from chemical analyses of already empirically understood bucking solutions or alkali samples. Certainly the discovery of acid washes released the production stranglehold caused by inordinately lengthy bleaching processes.

More importantly, it was from Home's quantitative method of determining the strength of blue ash and pearl ash by neutralization or "saturation," in which he used a teaspoon measure, that a branch of analysis had its origins. This was developed by William Lewis (46) and became known as titrimetry, so important in the future chemical industry.

REFERENCES AND NOTES

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2. Ref. 1, p 80. Charles Tennant (1768-1838) was a prominent Scottish bleacher. His method appeared in "A Table showing the Quantity of Soda (either free or combined with Sulphur or Carbonic Acid) contained in the Specimen under Trial with Sulphuric Acid containing 10 per Cent. real Acid...," *Ann. Philos.* (London), **1817**, *10*, 114 - 115. Barilla was the ash obtained by burning certain plants that grew freely along the Mediterranean shores.
3. F. W. Gibbs, ''Prelude to Chemistry in Industry," *Ann Sci.*, **1952**, *8*, 271-281; a review of the Clows' *The Chemical Revolution* (1952).
4. See W. A. Campbell, "Analytical Chemistry of the Leblanc Soda Trade," *Proc. Anal. Div. Chem. Soc.*, **1978**, *15*, 208-210, (208). John Mascarene of Cambridge, New England, was one notable exception; see F. G. Page, ''The Birth of Titrimetry: William Lewis and the Analysis of American Potashes," *Bull. Hist. Chem.*, **2001**, *26*, 66-72, footnote 7.
5. S. H. Higgins, *A History of Bleaching*, Longmans, Green & Co., London, 1924, 17.
6. S. Parkes, *Chemical Essays Principally Relating to the Arts and Manufactures of the British Dominions*, printed for the author and published by Baldwin, Craddock and Joy, London, 1815, Vol. 4, 23-26. Parkes gives a detailed technical and commercial account of bleaching practice in Holland and in the same volume refers to the work of Home. See also J. Horner, *The Linen Trade of Europe during the Spinning-Wheel Period*, M'Caw, Stevenson & Orr Ltd., The Linenhall Press, Belfast, 1920.
7. F. Home, *Experiments on Bleaching*, printed by Sands, Donaldson, Murray & Cochran for A. Kincaid & A. Donaldson, Edinburgh, 1756; 2nd ed. (containing the *Appendix* by Joseph Black), T. Ewing, Dublin, 1771, 16. The work by J. Dunbar, *Smegmatologia, or The Art of Making Potashes, Soap, and Bleaching of Linen*, Edinburgh, 1736, is probably the first publication on bleaching. See also J. R. Partington, *A History of Chemistry*, Macmillan, London, 1962, Vol. 3, 141.
8. Ref. 5, pp 23-26.
9. Ref. 1, p 79.
10. E. Musson and E. Robinson, *Science and Technology in the Industrial Revolution*, Manchester University Press, Manchester, 1969, Ch. III, section XII.
11. See Ref. 3, p 279.
12. G. Jardine, "Account of John Roebuck," *Philos. Trans.* (Edinburgh), **1796**, *4*, 65-87 (79).
13. J. Durie, *The Scottish Linen Industry in the Eighteenth Century*, John Donald, Edinburgh, 1979, 84.
14. Ref. 7, (1771).
15. Ref. 7, Black in Home, (1771), pp 267-282.
16. James Ferguson of Belfast, with whom Black discussed the use of lime in bleaching long before Black's paper appeared in Home's *Experiments on Bleaching*, (1771). See 'Ferguson to Black,' September 27, 1763, Edinburgh

University Library (EUL), Gen. 873/1/13,14 and 'Black to Ferguson' (replying) October 14, 1763, EUL, Gen. 873/1/9-11.

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18. L. Gittins, "Innovations in Textile Bleaching in Britain in the Eighteenth Century," *Business Hist. Rev.,* **1979**, *53*, 194-201, (201).
19. Ref. 7, (1771), pp 83-4.
20. Ref. 1, p 136.
21. J. Thomson, *Account of the Life, Lectures, and Writings of William Cullen, M.D.*, Blackwood, Edinburgh, 1832, Vol. 1, 76-9, in which the author reported on Cullen's "Remarks on Bleaching," written in 1755 for the Board of Trustees but not published. Located in the Scottish Record Office (Archives of the Board). Not seen.
22. Bucking: to soak or steep in alkaline solution; see A. Rees, *Manufacturing Industry,* David and Charles, Trowbridge, 1972, Vol. 1, 178; originally published as *The Cyclopaedia; or Universal Dictionary of Arts, Science and Literature*, *39* vol., 1802-1819.
23. Ref. 7, (Partington), p 141.
24. W. Ramsay, *The Life and Letters of Joseph Black, M.D.*, Constable, London, 1918.
25. S. M. Edelstein,'' Two Scottish Physicians and the Bleaching Industry, The Contributions of Home and Black,'' Part IX in ''Historical Notes on the Wet Processing Industry,'' *American Dyestuff Reporter*, **Sept. 26, 1955**, 681-684 (682). Reprinted in *Historical Notes on the Wet-Processing Industry*, Dexter Chemical Corporation, 1972, 35-38. The absence of documented evidence regarding communications between Home and Black is discussed on pp 35-36.
26. Ref. 7, (1771), pt. 3, section 1, p 64. The 1756 and 1771 account by Home is word for word identical. For convenience in referring to Black's contribution the 1771 edition has been used here.
27. Ref. 7, (1771), p 64.
28. Ref. 7, (1771), p 64, Exp. No. 14.
29. Ref. 7, (1771), p 82, and Exp. No. 27-34
30. Ref. 25, (1955), p 683.
31. Ref. 7, Black in Home (1771), p 268, "An Explanation of the Effect of Lime upon Alkaline Salts..."
32. Ref. 5, p 13.
33. L. Donovan, *Philosophical Chemistry in the Scottish Enlightenment: The Doctrines and Discoveries of William Cullen and Joseph Black*, Edinburgh University Press, Edinburgh, 1975, 79.
34. Ref. 7, Black, in Home (1771), par. 2, p 268, 278
35. Ref. 7, Black in Home (1771), p 277.
36. Ref. 7, Black in Home (1771), p 277.
37. Ref. 7, Black in Home (1771), p 277.
38. Ref. 7, Black in Home (1771), p 281.
39. Ref. 7, Home (1771), pp 55-6.
40. Dr. Eason, "Observations on the Use of Acids in Bleaching of Linen," *Memoirs and Proceedings of the Manchester Literary and Philosophical Society,* **1785**, *1,* 240-2. Ref. 24, pp 52-54.
41. Ref. 25, (1955), p 684.
42. The earliest mention that bleachers were to be prohibited from using lime occurred in 1633 and is recorded in *The Acts of the Parliaments of Scotland* (1625-1641). This and other similar acts of prohibition were first repealed in 1823. Higgins, Ref. 5, pp 13-16, cites a prosecution for using lime in 1815. See also Partington, Ref. 7, p 141.
43. Ref. 7, Black in Home (1771), p 271.
44. J. R. R. Christie, "The Origins and Development of the Scottish Scientific Community, 1680-1760", *Hist. Sci.*, **1974**, *12*, 122-141; also Donovan, Ref. 33; and M. P. Crosland, 'Rise and Fall of Scottish Science' in *Emergence of Science in Western Europe*, Macmillan, London, 1975.
45. Ref. 4, (Page).

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