AN 1815 PERSPECTIVE OF CHLORINE AS A CHEMICAL AGENT USED IN BLEACHING - A SECTION FROM JAMES RENNIE'S ESSAY ON BLEACHING

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Introduction

Among publications concerning the chemical properties and bleaching aspects of chlorine in early bleaching is included the analytical testing of bleaching solutions, as described in a manuscript entitled "An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry" by James Rennie (1787-1867). The manuscript is held by Birmingham City Archives within the James Watt Collection, and it is thought to have been written in 1815-16, very probably shortly before Rennie was awarded a first prize for this essay in the same period. The authorship is indicated by a pencil insertion in an apparently different hand. An edited but incomplete version was published as a series of articles titled "Essays on Bleaching, By James Rennie, A.M. Lecturer on Philosophy, &c. &c., London," in *The Glasgow Mechanics' Magazine; and Annals of Philosophy* during the period 1825-1826. For this present short article Rennie's section entitled "Chlorine and its Compounds," part of Chapter IV, "Chemical Agents used in Bleaching," has been fully transcribed; and it is within this chapter that Rennie covers his main chemical considerations within the entire essay.

This author first encountered Rennie when seeking evidence for the use of indigo in a test method to determine the bleaching strength of chlorine water solutions in the early bleaching industry in Britain. Such evidence was found in the essay mentioned above. Useful though this was, the present assessment will show little original material by Rennie, whose strength lay more in his accurate and wide reporting from established published sources of the period rather than from practical knowledge of the burgeoning Scottish industry. This single section of Rennie's *Jugendwerk* provides a systematic presentation of material, the whole of which qualifies the work more as a treatise than essay. This perhaps explains the several citations made by Musson and Robinson (1), these being the only modern historians of science to draw from this long forgotten, obscure manuscript. An account of Rennie's quite extraordinary life in Britain until his departure to Australia in 1840 is given elsewhere; but for contextual reasons some brief notes are presented here about his life up to the time of his writing the essay (2).

The Essayist: James Rennie (1787-1867)

The *Oxford Dictionary of National Biography* correctly describes Rennie as a naturalist, born February 26, 1787 (3), son of Thomas Rennie (or Rainey) of Alderholm, Sorn, Ayrshire, Scotland. Nothing is known of James' early years until his matriculation at Glasgow University in 1810 (4). He appears to have studied the standard arts curriculum, which included Greek, Logic, Ethics, Physics, and Latin; and it was during these undergraduate years that he won prizes for essay writing (5). After graduating in 1815 (6), he gained two further prizes: one for an essay on bleaching, the other for an essay on the use of steam in navigation (7). For each of these he was awarded the Watt Prize of £10. The only known complete copy of Rennie's bleaching essay is among the papers of James Watt, held by Birmingham City Archives. James Watt wrote to George Jardine of Glasgow College regarding essay prizes "to be given annually as a premium for the best Essay (by any student in the College) upon any subject in Natural Philosophy, Mechanism or Chemistry or the arts ... which shall be appointed by the faculty yearly ..."(8). Apparently, Watt proposed to donate prize money and suggested a five-yearly cycle of topics (9):

1. Bare mechanics, its machines & arts

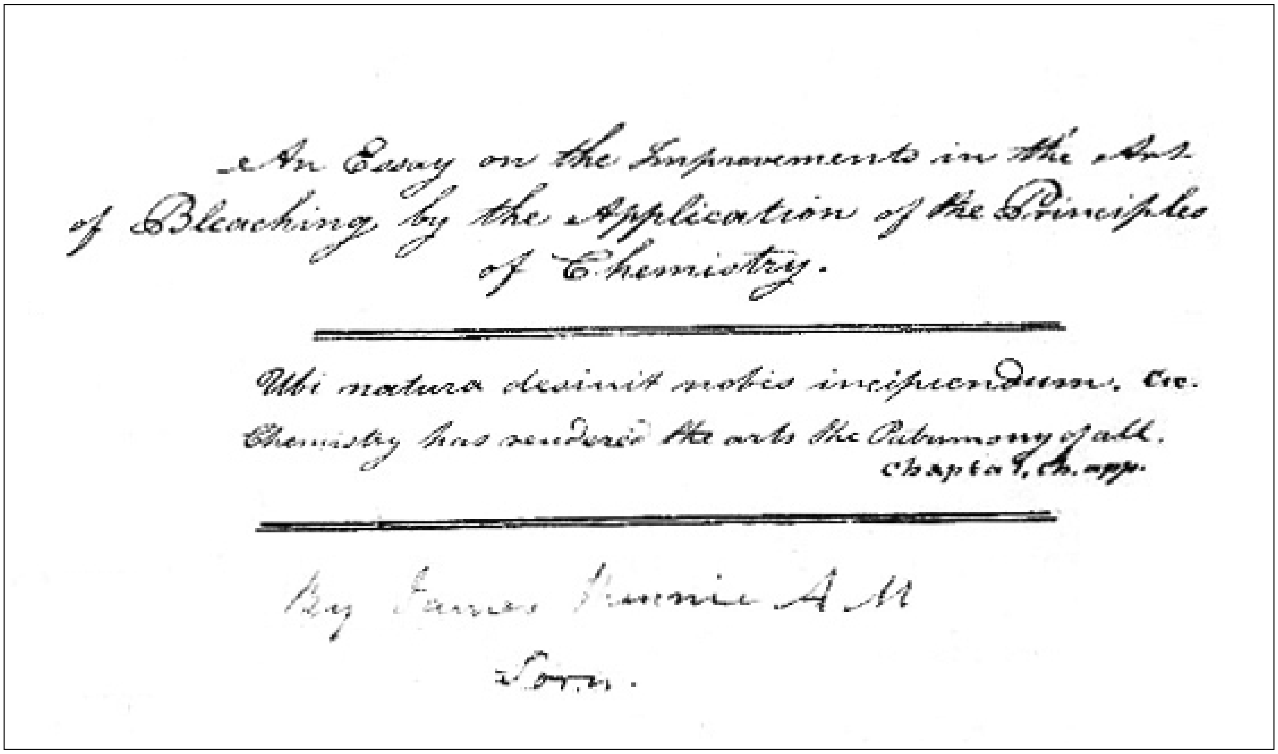
2. Statics, its machines & arts, Equilibrium of forces, weighing machines, Bridges, Carpentry, etc. etc.

3. Pneumatics, Statical and Chemical, Windmills, Sails, Bellows, Barometers, etc. etc.

4 Hydraulics and Hydrostaticks, Machines & Arts, canals, sea ports, mills,

5. Chemistry in general, & its processes & apparatus.

There is no evidence that Rennie continued as a registered student at Glasgow University after 1815, but it is possible that he may have taken classes on an informal basis. His essay writing in order to win financial reward appears to have been an acceptable activity of graduates of the period.


An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry.

Ubi natura desinit nobis incipiendum, &c.

Chemistry has rendered the arts the Patrimony of all.

Chaptal, Ch. app.

By James Rennie A M

"Chlorine and its Compounds:" Section 8 of Chapter IV, transcribed from the original manuscript.*

*Boldfaced endnotes in parentheses within the essay refer to those of the present author, as do square bracketed insertions.

Chlorine and its Compounds

Next to oxygen Chlorine is perhaps the most interesting of all the chemical agents. The theoretical researches to which it has given rise are the most profound and the least satisfactory of all the subjects of Chemistry. With these at present we have nothing to do; but we shall find its use in manufactures and chiefly in Bleaching no less interesting and surely more important than the ingenious theoretical discussions which it has produced (**10**). This substance has been called an acid, but it wants one of the most marked properties of this class of bodies, namely, the power of converting vegetable blues to red. Chlorine discharges all vegetable colours and renders them white; hence its use in Bleaching and its distinction from acids.

In the gaseous form it is of a greenish yellow colour, whence its name; and, although it supports combustion, it cannot be respired without great injury to animal life.

For the purposes of Bleaching it is made by an apparatus invented by Berthollet and subsequently improved by Henry, Des Charmes, Fisher, and others **(11).** A description of the latest improvements in this apparatus has already been given: I shall now briefly state the process. - The black oxide of manganese and muriate of soda are mixed together in the proportion commonly of 2 to 3, and after moistening them with water they are wrought till the mixture is of the consistence of moist dough, in order that the manganese may unite more intimately with the salt. The mixture is perfect when it is uniformly black. In this state they are put into the retort. There is now gradually added in conformity to the above proportions 2 2/7 [two and two sevenths] parts of sulphuric acid diluted with its own weight of water and allowed to cool in order to prevent accidents. This immediately without the application of heat disengages chlorine from the mixture in the state of gas. As soon as the quantity of gas thus disengaged diminishes, a fire is kindled under the water bath in which the retort is placed and continued till all the procurable gas comes over. This gas impelled by its expansive force passes from the retort to the large leaden receiver where it is combined with water, with lime, or with some of the alkalies. The rationale of this process is, that the sulphuric acid having a greater affinity than muriatic acid for the soda of the muriate, combines with the soda and sets free the muriatic acid which according to Davy parts with its hydrogen to the manganese; - according to the old theory attracts the oxygen of the manganese, - forming chlorine gas. This gas it was, which was formerly used in Bleaching pure and without admixture; but this is now, I believe, wholly laid aside: and a combination of it with water - potash - soda - magnesia - or lime; is preferred. These it will be necessary to discuss in their order.

1. The chlorine diffused through water was the mode of using it invented by Berthollet, and still followed in some old establishments. The Bleaching liquor formed in this way may be either made of the proper strength for use at first, or it may be made stronger and more concentrated by putting in a smaller quantity of water into the receiver or a larger proportion of ingredients into the retort; in which case it can be afterwards diluted to the proper strength. When the liquor is much concentrated it has, like the gas, a greenish yellow colour or what Werner calls a siskin green **(12).** It has also like the gas a very penetrating and offensive smell arising indeed from the disengagement of the gas. It cannot be breathed even for a few instants, without the danger of a most obstinate and violent cough; and it sometimes causes the workmen to fall down senseless. Asthmatic affection of the breast, headache, tears and smarting of the eyes, bleeding at the nose, pains in the small of the back, and spitting of blood are the ordinary symptoms which its respiration induces. So that unless the most careful and unremitting attention be paid to the lutes, it is impossible even for a strong man to support for several successive days so unhealthful an employment. Des Charmes (Page 65.) **(13)** was so much affected by the violent expectoration this produced, that he could retain no food on his stomach; he was deprived of sleep and exceedingly afflicted with acid humours flowing from his nose and eyes so that he could not bear the light, while he suffered great pain in his back and thighs. These consequences are very serious and they soon called forth the genius of invention to contrive preventives. One of these was to introduce carbonate of potash or soda into the water in the receiver in the proportion of one fourth to one of the muriate of soda employed. Even the sprinkling of a solution of any of those carbonized alkalies upon the surface of the Bleaching liquor previously to using it, will in a great measure neutralize the disagreeable effluvia. By this method however the alkali was not only totally lost and the expense in consequence greatly increased, but the detergent power of the liquid was supposed to be considerably diminished which was attempted to be proved by Mr. Rupp of Manchester from numerous experiments **(14).**

To obviate the primary evil, and to avoid the expense of its proposed cure he contrived a very simple apparatus for exposing the goods equally to the liquid and preventing the escape of the noxious gas, a description of which has already been given in its proper place. The application of Chlorine condensed in water however may now be considered as one of the nearly obsolete agents in Bleaching, although it is unquestionably more powerful than any of the oxymuriates.

2. When the simple gas, and also water impregnated with it were mostly given up, oxymuriate of potass or soda came to be used as we have already seen in the history. The preparation of the Bleaching liquor with these is precisely similar to that employed in the impregnation of water: the leaden receiver being in the former case filled with a solution of one of these alkalies. The experiments of Mr. Rupp and others, to prove that the detergent power of Chlorine is diminished by neutralizing it with an alkali, have been found practically erroneous. It is not unlikely

indeed that they were deceived by the circumstances of the oxymuriates not producing so sudden an effect as the pure chlorine, but this is rather an advantage than otherwise, for the chlorine is disengaged so slowly and gradually from these salts that time is given it to act equally and effectually on every part of the cloth. Little is lost consequently by the escape of gas which is so copiously emitted in the former case; and the operation is also rendered more healthy to the workman. Lately, the combination of Chlorine with the mineral alkali has been much used in the Calico manufacture for clearing the whites of maddered goods, and it has almost superseded, in this department of the art, the tedious and expensive process of crofting. It is used in a state of great dilution; for although a strong solution would clear the whites more rapidly and more effectually, yet care must be taken not to make it strong enough to affect the colours which are to remain fast in the piece. The strictest attention ought to be paid to the purity of the alkali used for making oxymuriates, as if it be contaminated with neutral salts, the chlorine is not all taken up, and that which is left in an uncombined state being greatly stronger than what unites with the alkali, it will attack the colours of the printed goods, and in all probability discharge them.

3. Sir Humphrey [*sic*] Davy found by experiment (Elem. of Chem Phil. I. 242-3.), that the texture of linen was considerably injured when immersed in a hot solution of chlorine and water by the corrosion as he supposes, of the muriatic acid **(15).** Now this he justly thinks decreases considerably the advantage of the speedy and effectual Bleaching which is thus produced. To remedy this he instituted a set of experiments and was so fortunate as to discover a substitute wholly free from this inconvenience, namely, the oxymuriate of magnesia. This may be produced by the method already described, by diffusing the magnesia through the water in the receivers with which the chlorine combines and becomes condensed. It acts much more slowly and gradually than any of the other compounds of chlorine employed for the same purpose **(16),** and consequently must produce a more equal detergency. At Sir Humphrey [*sic*] Davy's suggestion, it was employed to some extent for clearing the whites of printed calicoes, in the large establishment of Mr. Duffy of Dublin **(17),** and with great success, for it was not found to injure in the least even reds and yellows which had been fixed by mordants. While the oxymuriate of lime not only changes all the colours and renders them of a duller hue, but also particles of the lime attach themselves so intimately to the cloth that it acts as a discharge and effaces the colours altogether **(18).** The oxymuriate of potass again, although not so strong an alternative changes red to pink and gives to purple and lilac a bluish shade; the alkali always diminishes the intensity and brilliancy of all colours. The oxymuriate of magnesia seems free from these imperfections. Sufficient quantities of magnesia can be procured for this purpose from sea water or from the residual liquor of salt works; and perhaps the act which grants a drawback on salt to the makers of chlorine (38th Geo. III. c.89. s.89,) **(19)** may be found to extend to this use of sea water, or if not, that a similar act may be procured to pass when the advantage becomes manifest. It is not unlikely, if the oxymuriate of magnesia shall come into general use, that a similar method will be taken to manufacture it in the dry state as is now successfully practised with respect to the oxymuriate of lime, in order to facilitate its conveyance to a distance.

4. Lime was impregnated with chlorine for the purposes of Bleaching at an early stage of the improvements we are now detailing, by Watt, Henry, and Cooper, but it does not appear, that it was by them brought into their general practice, as they seem to have preferred the simple water or oxymuriate of potass. It was reserved for Mr. Charles Tennant of Glasgow to improve the process of making it so as to render it both a cheap, convenient, and efficacious agent in Bleaching. The oxymuriate of barites and strontites, which were also mentioned in his patent, were found to be too expensive for practical purposes, as the latter substance could not be procured in great quantity and the former could with difficulty be separated from the sulphuric acid, with which it is usually found combined. The first process which he adopted for the purpose was to dissolve 30 lbs. of muriate of soda in a receiver which contained 140 winegallons of water for this purpose of giving greater specific gravity to the water. The muriate being dissolved 60 lbs. of quicklime were added in the state of an impalpable powder. For the production of the gas, a retort was charged with 30 lbs. of pulverized manganese mixed with an equal weight of muriate of soda to which 30 lbs. of sulphuric acid, previously diluted with 18 lbs. of water, were added. The distillation was then conducted in the usual way, care being taken constantly to agitate the materials during the process. Mr. Tennant was deprived of the patent he had for the manufacturing of this substance in consequence of a decision of the court of session. The loss of his patent stimulated him to new efforts of ingenious invention, and he succeeded in combining chlorine with lime in the dry way, which renders it so easily portable to any distance at a small expense. In consequence of this his business

has increased very much, while the Bleaching processes have received great improvement. The expense also is greatly lessened, as lime is so much cheaper than the alkalies which wont to be consumed for this purpose to a prodigious amount.

In order to produce this important agent, the chlorine gas is sent into a receiver similar to that formerly described, which contains in a pulverized form the dry hydrate of lime, that is, lime slaked with the least possible quantity of water. The powder, during the influx of the gas from the distilling apparatus, is continually agitated and the gas combines with it to a certain amount or till the hydrate becomes saturated. The salt so formed is a soft white powder which possesses little of that intolerable smell so characteristic of the gas. It is partially soluble in water and its solution is little different from that obtained by the process in which the combination is formed in the solution of lime in water. So great has been the reduction of expense from the introduction of this agent, that it was proved upon oath, that by using it the consumption of ashes in a single Bleach-field has been reduced £3000 in value in one year.

The concrete oxymuriate of lime or Tennant's salt, as it is called by the Bleachers, is, when prepared for immediate use, diffused by agitation in a quantity of water. This is allowed to stand for some time till any insoluble matter contained in the lime be precipitated and the supernatant liquor remain transparent. The liquor thus clarified is drawn off and diluted with a considerable proportion of water, when it is ready for the immersion of goods. This salt differs remarkably from most others, that it cannot be procured from the solution either in a dry mass or in crystals by evaporation; for when such a solution is evaporated part of the acid escapes and the rest is mostly converted into muriatic acid; so that instead of oxymuriate of lime, muriate of lime is obtained. The dry salt can only be obtained by Mr. Tennant's process of using dry hydrate of lime in the first instance.

In treating of the other agents of Bleaching, we have seen of how much importance it is to the Manufacturers to be able to ascertain the quantity of efficient matter in any of the substances of commerce which he has occasion to purchase. With respect to oxymuriate of lime, this ought perhaps to be still more attended to, in so much as it is the principal agent for producing pure whites. But I am not aware that any method has come into general use among Bleachers, by which the quality of a given quantity of this substance can be ascertained. They are under the necessity indeed of ascertaining the Bleaching power of the diluted liquid previous to immersing their goods which is commonly done by an indigo test, and in this way by observing the quantity of salt and the proportions of water used they may make a crude guess concerning the strength of the salt when purchased, but this at best must be an inaccurate method of proceeding. To remedy those inconveniences, the ingenious Mr. Dalton instituted a course of experiments in which he was successful in obtaining a test of easy application for ascertaining the purity of Oxymuriate of lime. Of these experiments I think it of some importance in an essay of this kind to give a full and distinct account: I shall do so *in the author's own words*, promising that his explanations of the Phenomena are made upon the old theory that oxymuriatic acid (chlorine) consists of muriatic acid and oxygen **(20).**

> Experiment. 1. One Hundred Grains of recent dry oxymuriate of lime were exposed to a low red heat in an iron spoon: The loss was 32½ grains. To the residuum water was added, and a solution of 535 grain measures of 1.055 sp. grav. was obtained, and further an insoluble residuum of 30 grains. The solution was found to be muriate of lime, and consequently consisted of 16 muriatic acid and 18 of lime. The residuum was dissolved in muriatic acid, and formed a solution indicating 21 lime; a small portion of carbonic acid was given off, but not of any amount. No trace of oxymuriatic acid could be found after the salt had been heated. Hence we learn, that 100 grains of dry oxymuriate of lime contains 39 grains of lime, combined and uncombined; and that by a low red heat, all the oxymuriatic acid is either driven off or converted into muriatic acid.
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> Experiment. 2. One hundred grains of the same specimen of oxymuriate were added to upwards of 1000 grains of water; after being stirred for some time, the liquid was filtered, and 1000 grain measures were obtained of the sp. grav. 1.034; I got also a residuum, which, dried in a moderate heat, gave 33 grains. This last treated with muriatic acid was dissolved, and indicated 18½ lime. The liquid, which contained a mixture of oxymuriate and muriate of lime, was treated with carbonate of soda, which converted the whole of the lime into carbonate of lime. From the quantity obtained, it appeared that the combined lime in the liquor was also 18½ grains. From this experiment the total quantity of lime in 200 grains of dry oxymuriate was 37 grains. In the former it was 39 grains. The quantity of lime in the solution being thus found, it remained to find the quantities of muriatic acid and oxymuriatic acid with which it was combined. The muriatic acid was determined as follows.
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> Experiment. 3. Two hundred grain measures of a solution of the sp. grav. 1.034 were taken; to these a

given quantity of muriatic acid test was added, such as previous trials had shown was more than sufficient to expel all the oxymuriatic acid from the lime. The new compound was well agitated in a bottle, and the oxymuriatic acid gas was blown away as long as any continued to be given out. The liquid solution was then tested, and found to be acid, but not to destroy colour. Nitrate of mercury was then added, as long as any calomel was thrown down. The calomel, when dried, weighed 31 grains; one ninth of this was muriatic acid equal to 3.44 grains; and from this deducting the quantity of 2.14 grains added to the liquid there remain 1.3 grains of muriatic acid previously in combination with the lime. Now we have seen that the lime in 200 measures of liquid was 3.7 grains, which would require 3.5 grains of muriatic acid; it had previously only 1.3 grains; therefore the lime in combination with oxymuriatic acid must have been so much as would require 2.2 grains of muriatic acid to saturate it. Hence it appears, that nearly 1/3 of the lime in the solution was engaged by muriatic acid, and the remaining two thirds by oxymuriatic acid. But the quantity of this last was still undetermined.

The usual way of comparing the values of any two Bleaching liquids has been, I believe, to find how much of any given coloured liquid a given portion of the acid liquor would saturate. The experiment serves well for the purpose of comparison; but it does not inform us of the precise quantity, either of volume or weight, of the acid gas which the liquor contains. We might expel the acid gas from a given weight, either of the dry or liquid oxymuriate, by means of an acid, in a graduated tube, over mercury or water; but unfortunately both these liquids act upon the acid: no doubt the analysis might be accomplished this way; but it would require an apparatus expressly for the purpose. I have succeeded however another way in discovering a very excellent test of the quantity of oxymuriatic acid in any compound. This test is a solution of green sulphate of iron. As soon as green sulphate of iron comes in contact with oxymuriatic acid solutions, the black oxide is converted into red, at the expense of the oxygen of the oxymuriatic acid; if the sulphate is deficient, a strong smell of oxymuriatic acid accompanies the mixture; whence more sulphate must be added, till the mixture, on due agitation, ceases to emit the fumes of the oxymuriatic acid; if too much sulphate be put in, then more of the acid liquor must be added by degrees, till its peculiar odour be developed & a very few drops of either liquor are sufficient to give the mixture a character when near the point of saturation. I found that 40 grain measures of a solution of sulphate of iron of the sp. grav. 1.149 were sufficient to saturate 100 measures of oxymuriate of lime of 1.034 sp. grav. In order to understand more clearly the relative weights of oxymuriatic acid and oxide of iron, which are required for mutual saturation, I made the following experiment.

<u>Experiment</u>. 4. A graduated tube was filled with oxymuriatic acid gas. This was then plunged into a dilute solution of green sulphate of iron and the whole of the gas was by due agitation immediately absorbed by the liquid. If any smell of oxymuriatic acid remained, the experiment was repeated on a stronger solution of green sulphate; but if no smell remained, then it was repeated with a weaker solution; till in a few trials the strength of the sulphate was found, which was just sufficient to cover the smell of the gas; or in other words to saturate the acid. This was when the solution was 1.0120 sp. grav. or nearly 1/12 of the strength which I commonly use as a test solution, as mentioned above. Now 100 measures of oxymuriatic acid gas weigh .29 of a grain, reckoning its specific gravity at 2.46; and 100 measures of the sulphate contains (as I find by experience) 1.32 gr. of real dry salt, of which 68 pts are sulphuric acid and 64 pts oxide of iron; of which 50 are iron and 14 oxygen, as is well known. The red oxide of iron is known to contain half as much more oxygen as the black; hence 64 pts. of black oxide will become 71 of red, or the black oxide receives 7 pts. of oxygen from the 29 of oxymuriatic acid, and reduces it to 22 of muriatic acid. These numbers perfectly accord with those deduced as the weights of the respective atoms. (Dalton's Phil. of Chem. P.^{t} II.). [Dalton wrote "in the 2d part of my chemistry." *Rennie leaves out a small section here of Dalton's paper and now quotes only selectively*.] We conclude that dry oxymuriate of lime contains in 100 parts, 13.5 muriate of lime, 26 oxymuriate of lime, 18.5 lime, and 42 water **(21).**

Mr. Dalton adds, that age diminishes the value of a solution of oxymuriate of lime, by converting it partially into muriate; but this effect is also produced in some degree on the dry salt when kept in a bottle. He had kept some in this manner for 6 years which was at first about the same value as that whose proportions have just been stated: he found it so far depreciated as to contain only 1/4 or 1/5 of the requisite quantity of oxymuriatic acid. (Ann. of Phil. I. 20.) **(22).**

Although however the green sulphate of iron appears from these experiments to be by far the best test of the oxymuriate of lime, yet as the indigo test does tolerably well in ascertaining the strength of the diluted liquor, and as it is very generally used, I cannot well omit detailing the manner of its application. Prepare a very dilute solution of indigo by dissolving in the usual way a pound of the best Spanish in four pounds of concentrated sulphuric acid, which proportions will generally be sufficient to produce saturation. When all the indigo is dissolved one part by measure of this solution is to be diluted with sixteen parts by measure of water, when it will be fit for use. To

> obviate any deception which may arise from the difference of strength in the indigo, it is best always to preserve some of a former preparation to compare with the new, when by a little management it may be made equal. The quantity of water used is not material provided that the same Bleacher keep always to the same proportion. The strength of the Bleaching liquor is determined by the quantity of it which is required to destroy the colour of any given portion of the test. In practice it is usual to have two graduated glass tubes, one for the test the other for the liquor, by which arrangement the efficient quantities are seen by inspection **(23).** Berthollet says (Ann. de Chim. II.) he was informed by Mr. Watt, that the indigo test will not accurately show the strength of either oxymuriate of soda or of potass, and recommends a decoction of cochineal as not being so liable to inaccuracy or deception **(24).** From what I can learn however, this has not been found so convenient in practice as the indigo test: Mr. Dalton's test from sulphate of iron will soon, I imagine, supersede all others. (see Page, 172-3) **(25).**

Concluding Remarks

In this article only 18 pages from Chapter IV of Rennie's essay, consisting of 213 pages (26), have been considered. Any cautious conclusions therefore arise from this small sample only. It is clear that the writer drew extensively upon published works for his information. Source acknowledgments are not consistent and in some instances are completely missing. His choice of subject was fitting, particularly if only because the role of chemistry in industry was becoming apparent in the rapidly expanding field of bleaching.

Elsewhere in the essay Rennie stated that he did not envisage its publication, although he probably wrote the work in the hope of financial reward. Such hope was realized for it has been shown that the prize of £10, a considerable reward, was gained,. The author was a highly educated and well read postgraduate, well-versed in the art of successful essay writing. His two other prize-winning essays attest to this ability and to his potential as a future writer. That potential was indeed realized but is outside the scope of this article.

The manuscript of the essay bears no date, but the fact that it is headed "By James Rennie A.M." suggests it was composed in 1815 (his graduation year) or shortly afterwards; and this is further confirmed by the award of a prize in 1815–1816 (27). Thus Rennie was 28 years old and unmarried when he wrote it. Whether or not he aspired to a career in writing and lecturing cannot be ascertained, although this proved to be his main employment some years later. He held the professorship of natural history at King's College, London from 1830 to 1834.

For this essay he drew freely on other contemporary authors of reputable standing, particularly in matters of chemistry. It should be noted that textbooks of that time often contained sections devoted to the art of bleaching. For example, Parkes's *Chemical Essays* contains a considerable treatise entitled "Bleaching," which most certainly assisted Rennie in writing his essay (28). His several references elsewhere in the essay to Thomas Thomson are noteworthy. Clearly *A System of Chemistry* (29) was very well known and Rennie appears to have held its author in the highest esteem by recalling, many years later, of the …"'highly distinguished chemist, Dr. Thomson, whose pupil I also had the good fortune to be" (30). The entry on bleaching in *Encyclopaedia Britannica* (1803), possibly by Thomson, may have induced Rennie to take this subject as the basis for his own essay (31). Rennie's evident plagiaristic use of the *Edinburgh Encyclopaedia* (1811) has been noted in earlier sections of the essay and interestingly, though not reported by Rennie, it is from this source that we first learn of Watt's full scale trial involving chlorine bleaching of 500 pieces of linen (32).

As a future professor of natural history the essay-writer was also a reputable chemist, having clearly informed himself of many aspects of the subject. It seems a pity that he chose to quote verbatim such large tracts of other people's work, sometimes without giving specific acknowledgment. Nevertheless, this points to his unquestionable knowledge of the standard and most recent literature. Certainly Rennie's *Jugendwerk* on bleaching remains an exemplar of what was known (chemically) and practiced in the period before its writing in about 1815 and clearly points to his abilities and potential as an author.

This small chapter about chlorine points to Rennie's close use of contemporary textbooks and journals. For example, bleachers' dependence upon elemental chlorine, often generated on their own premises, had probably diminished at the time he wrote the essay—a point not yet evident in published books of the time—although Rennie recognized the process as being obsolete. The new bleaching powder available from the developing manufacturing of Charles Tennant Company of Glasgow (33) was reported by Rennie, but he failed to present this as a far more satisfactory means of obtaining a bleaching solution. So by 1815 the generation of elemental chlorine gas and its dissolution in water or alkaline solutions by individual textile firms had greatly diminished. Bleachers were turning to the use of bleaching powder. Though discussed by Rennie, particularly the methods used to determine its strength in bleaching operations, he nevertheless presented the older methods of using elemental chlorine in some detail.

Regarding Rennie's analytical observations, it is difficult to see why he chose to give John Dalton so much attention. Dalton's analytical methods, accurate though these were, must nevertheless have been quite inappropriate to the limited laboratory resources and chemical knowledge of the time. The lengthy and complicated methods offered no advantage in an industrial context at a time when faster volumetric determinations were becoming popular. Furthermore, through the introduction of solid bleaching powder, a measured weight or volume would result in a roughly judged bleaching strength, the bleaching operative merely needing confirmation by the simplest of tests: the indigo test.

During the twenty-five years following the appearance of this essay Rennie continued a successful writing and lecturing career in Britain, before leaving for a new life in Australia in 1840. The essay and the small section considered in this article concerning chlorine bleaching remain as testament to his early abilities.

REFERENCES AND NOTES

1. A. E. Musson and E. Robinson, *Science and Technology in the Industrial Revolution*, Manchester University Press, Manchester, 1969, 261, footnote and other references throughout chapter VIII, "The Introduction of Chlorine Bleaching."
2. F. G. Page, "James Rennie (1787-1867), Author, Naturalist and Lecturer," *Arch. Nat. Hist.*, **2008,** *35,* (1), 128-142.
3. J. Hodge, "James Rennie (1787–1867)," *Oxford Dictionary of National Biography*, Oxford University Press, Oxford, 2004. http://www.oxforddnb.com/view/article/23375, accessed Sept. 20, 2006].
4. W. I. Addison, The *Matriculation Albums of the University of Glasgow from 1728-1858,* J. Maclehose, Glasgow, 1913. In this year, 1810, he was in the class of John Young, Professor of Greek. His father's name is given as Thomas, an Ayrshire farmer.
5. Noted in the University Prize Lists for the period 1777-1833, compiled by W. I. Addison, Glasgow University Archives (GUA) R7/1/1. Logic 1811-12, Ethics and Logic 1812-13, Mathematics and Physics 1813-14; these were class prizes, value unknown but probably less than £10. It was during 1814-15 that he gained a prize for a geology essay, "A Comparative View of the Huttonian and the Wernerian Theories of the Earth," handwritten, signed by James Rennie, A.M., Glasgow. 1815; [George Neilson Collection of MS, author of *Trial by Combat* and joint editor of *Acta Dominorum Concilii*, *1496-1501*, Edinburgh, 1918.] The National Library of Scotland (hereafter NLS) acquired the collection in 1927, and there is no indication in the MS as to how Neilson obtained the copy of the essay. The essay contains a pasted page (vi) insertion: "To the Most Noble The Marquis of Douglas and Clydesdale with J. Rennie's most grateful and respected Compliments - Glasgow College 18th April 1816." The hand does not appear to be that of Rennie. This essay gained second prize, donated by a Mr. Coulter. The first prize, donated by Dr Watt of Birmingham, was awarded to George Oswald Sym of East Kilpatrick.
6. W. I. Addison, *Roll of Graduates of the University of Glasgow 1727-1897*, Maclehose, Glasgow, 1898. The Register of Masters of Arts for 1764-1888 (GUA 26676) records Rennie's graduation on July 20, 1815. The listing also noted: 'Professor of Natural History at Kings College London, 1830-34; emigrated to NS Wales, 1840, born at Sorn, Ayrshire 26 February 1787; died at Adelaide, 25 August 1867.'
7. "An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry," [Birmingham City Archives (BCA), MS 3219/4/295, formerly JWP/C4/C8.] This was followed by another prize winning essay: "Essay on the Application of Steam to the Purposes of Navigation," 1816, [NLS, MS 9352.] Both essays were awarded the Watt prize (£10).
8. BCA James Watt Papers, Private Letters 1803-10, p 219, to Geo Jardine Esq., Coll., Glasgow April 26, 1808.
9. Ref. 8, p 225, to James Young, Coll. Glasgow, June 4, 1808. It is not clear into which part of this cycle Rennie's essay fitted.
10. Rennie could be referring to the lengthy controversy over whether chlorine contained oxygen and was truly elementary. Davy had argued in 1807 that chlorine (oxymuriatic acid) contained no oxygen, but others, such as Gay-Lussac and Berzelius, believed otherwise. One strong voice supporting the nonelementary nature of chlorine was that of John Murray (d.1820), to whom Rennie had referred in an earlier section of his essay. Rennie appears to show little regard for these theoretical arguments and places the value of chlorine entirely in its practical bleaching properties.
11. Berthollet's first publication about chlorine and its bleaching effects was reported to the Académie Royale des Sciences in 1785 followed by a more practical article in *Ann. Chim.*, **1789**, *2*, 151-90. Berthollet's apparatus is fully described in the translation by R. Kerr, "Essay on the New Method of Bleaching by means of Oxygenated Muriatic Acid...from the French of Mr. Berthollet," Edinburgh, 1790, published by Order of the Trustees of the Linen and Hempen Manufacture, unnumbered page preceding, p 130 and pp 130-139. In 1794 Peter Fisher of Glasgow designed the apparatus described in *Edinburgh*

Encyclopaedia, 1811, Vol. 3, 579. A footnote indicates that Fisher's apparatus was essentially the same as that of Charmes and Berthollet.

12. Rennie's reference to A. G. Werner is not unexpected although of little importance in this instance. The bleaching essay and a further prize winning essay, "A Comparative View of the Huttonian and the Wernerian Theories of the Earth," (see Ref. 5) were written in the same period. He clearly had some knowledge of Werner's writings, but it is impossible to decide whether Rennie had referred to Werner's own German publications or the translations by Robert Jameson, "A Treatise on the External Characters of Minerals," 1805 and 1816, by several publishers, Edinburgh and London. In the 1805 edition on p 11: "*Siskin green* is emerald green mixed with lemon yellow and a little white. It makes the transition to the yellow colour…" Interestingly, the *OED* ascribes the first use of this color description to James Robertson in 1805.
13. C. Pajot des Charmes, *The Art of Bleaching Piece-Goods Cottons and Threads...*, G. G. & J. Robinson, London, 1799, a translation by W. Nicholson of *L'Art du Blanchiment des Toiles, fils et cotons de tout genre*, Paris, 1799. Charmes' vivid description of the results of the toxicity of oxygenated muriatic acid (p 64) states: "It cannot be breathed even for a few instants, without the danger of a most obstinate and violent cough. Its action is sometimes so strong that the operator will fall down senseless…"
14. T. L. Rupp, "On the Process of Bleaching with the Oxygenated Muriatic Acid; and a Description of a New Apparatus for Bleaching Cloths with that Acid Dissolved in Water, without the Addition of Alkali," *Mem. Manchester Lit. Philos. Soc.,* **1798**, *5*, 298-313. Rupp reported that the addition of alkali increasingly reduced the decolorizing property. This was a misleading statement, but it appeared to support Berthollet's ideas. See also J. G. Smith, *The Origins and Early Development of The Heavy Chemical Industry in France,* Clarendon Press, Oxford, 1979, 136-139.
15. H. Davy, *Elements of Chemical Philosophy*, 1812, J. Johnson, London, Vol. 1 (pt.1),; Davy mentions a warm solution only (p 242).
16. Ref. 15. This is an exact quotation from p 243, and the following sentence is almost word-for-word the same as Davy's text.
17. Duffy, Bryne, and Hamil Company, a staining and printing firm active into the early decades of the nineteenth century.
18. This sentence is word-for-word the same as in the *Edinburgh Encyclopaedia,* Blackwood, Edinburgh, 1811, (pt. III & IV), Vol. 3, 577-591 (587, note 64).
19. 38th George III. cap. 89. (1798) "An Act for Transferring the Management of the Salt Duties to the Commissioners of Excise," is a major Act embracing the entire salt duties legislation. It includes the use of salt in the production of synthetic alkali and chlorine for bleaching and their byproducts, and extends to 30 pages. Section 89 refers to "A drawback of duties to be allowed on British salt used in making Oxigenated Muriatic Acid for bleaching linen," and contains the statement that salt had to be "mixed with vitriolic acid, manganese and water, in the presence of the proper Officer of Excise...nor should any such drawback or allowance be granted to any person not being an actual bleacher of linen or cotton;" section 89 appears to have no relevance to sea water or residual liquor of salt works (bittern).
20. This is indeed full credit to Dalton; however, Rennie has drawn word-for-word from John Dalton, "On the Oxymuriate of Lime," *Ann. Philos.* **1813,** *1,* 15-23. Rennie's remark about Dalton's adherence to "the old theory" of the composition of oxymuriatic acid gas is noteworthy insofar as their writings were separated by only two years. It is this paper that contains Dalton's method of determining the strength of oxymuriate of lime by using the reaction with ferrous sulphate solution (Experiments 3 and 4), a method supported by Rennie in his closing remark (but probably rarely used).
21. Ref. 20, p 19.
22. Dalton reported on a further three experiments, but Rennie has ignored them. The case for using the ferrous sulphate test, rather than one based on a simple color change, is strongly argued by Dalton.
23 Rennie gives no credit to F. A. H. Descroizilles as the inventor of this important analytical test. The method was first brought to public notice by Claude Louis Berthollet, *Essay on the new method of bleaching, by means of oxygenated muriatic acid; with an account of the nature, preparation, and properties, of that acid. ... From the French of Mr. Berthollet. ...* by R. Kerr, ..., Trustees of the Linen and Hempen Manufacture, Dublin, 1790, 80. A quotation from the 2nd ed. (Edinburgh, 1791), p 131, is as follows: "Mr Decroisille [Descroizilles] has contrived a test, or gauge, by means of a solution of indigo in sulphuric acid. He takes one part, by weight, of indigo, reduced to a fine powder, with eight parts of concentrated sulphuric acid, and digests this mixture in a matrass, exposed to a sand heat for some hours, until the indigo is completely dissolved by the acid. This solution is then diluted with one thousand part of water, and is to be employed for measuring the force of the oxygenated liquor,…"I have not identified from where Rennie obtained his information. Spanish indigo, usually from Guatemala or Mexico (both countries were part of the Spanish empire), regarded as superior to African or SE Asian indigos, was widely available, if expensive. It was not however specified by Descroizilles. Furthermore, why Rennie suggested an indigo concentration of more than 1% is difficult to explain when Descroizilles had recommended 0.1%. Descroizilles' own account of this first volumetric method appeared as "Description et usages du Berthollimêtre," *J. Arts Manufactures*, **1795, 1**, 256-276, although the underlying idea had been mentioned earlier by Berthollet.
24. There is little evidence to show that cochineal was ever used in preference to indigo. Watt's first recommendation

for its use appeared in a letter dated February 15, 1788 to his father-in-law, Mr. McGrigor (MS 239, Birmingham City Archives); but the suggestion was not pursued and the indigo test continued to be used. Berthollet's report on Watt's suggestion appeared in *Ann. Chim.*, **1789,** *2*, 151-190 (188).

25. There is little evidence that this test gained common use. It was mentioned by S. H. Higgins, *A History of Bleaching*, Longmans, Green, London, 1924, 93, who described the Stockport bleach works of Sykes & Co: "Bleaching powder was tested at Sykes: in 1845 by titrating with sulphate of iron until the liquor changed red to yellow prussiate of iron." See also F. Szabadváry, *History of Analytical Chemistry*, Pergamon Press, Oxford, 1966, 217: "This rather uncertain method, however, was used for quite a long time,.."
26. The dimensions of the hand written volume are as follows: height 250 mm., width 205 mm., depth 21 mm. It contains 114 leaves and the volume consists of page numbers 1-213, along with an introduction page, contents pages, and the title page. The paper used is of a good heavy quality and is watermarked "J Budgen 1815."
27. W. I. Addison, *Glasgow University Prize Lists 1722-1833*, Carter & Pratt, Glasgow, 1902.
28. S. Parkes, *Chemical Essays,* Baldwin Cradock and Joy, London, 1815, Vol. 4, 3–177.
29. T, Thomson, *A System of Chemistry,* Bell & Bradfute, Edinburgh, 1802, 4 vol.
30. *Alphabet of Scientific Chemistry for the Use of Beginners*, W. Orr, London, 1833, xi.
31. T. Thomson, "Bleaching," *Supplement to the Encyclopaedia Britannica*, Thomas Bonar, Edinburgh, 1803, Vol. 1, 80-88.
32 *Edinburgh Encyclopaedia*, Ref. 18, Vol. 3, footnote on p 578.
33. See E. W. D. Tennant, "The Early History of the St. Rollox Chemical Works," *Chem. Ind. (London)*, **1947**, 667-673 (669). In the period 1799-1800 Tennant produced 52 tons of bleaching powder and in the following five years the amount trebled. By the time Rennie wrote the essay, output was probably approaching 300 tons annually or more. Clearly the change from chlorine water/alkali solutions to solid powder was underway by 1815.

ABOUT THE AUTHOR

Dr. Frederick G. Page, Wychbourne Kington Herefordshire HR5 3AQ. UK, after gaining a doctorate under the supervision of Professor William H. Brock at University of Leicester in 1999, has continued to publish and research topics related to his thesis regarding early analytical chemistry in the bleaching and alkali industry. He is currently transcribing the essays of James Rennie, author, naturalist, and lecturer; a small section of one of these being the subject of the above article.