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SOME
EARLY EXAMPLES
OF
PLANT DEVELOPMENT
AND
PROCESS CONTROL
IN THE
CHEMICAL INDUSTRY

Thesis presented for the degree of
Master of Science in the
University of Durham

by

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Durham



September 1977

ABSTRACT

Seventeenth century alum works were organised rationally and operators used physical and chemical tests to evaluate raw materials and to give necessary information for control of the process.

Managers of the Boulby and Loftus plants during the second half of the eighteenth century and the first half of the nineteenth century continued to use these tests and developed their application to control of the preparation of Kelp for the process and in evaluation of newer raw materials which replaced Kelp.

A works laboratory was in existence at Loftus from 1805 and from 1820 a library of "sound" chemical text^s was maintained on the plant. Process development evaluation; process investigations; systematic investigation of Faraday's recommendations were carried out in addition to basic tests. The works chemist's function emerged.

The large workforce was given specific tasks and salary and/or rates of pay indicated both a seniority and a succession. Details of the method of operations, which remained essentially unchanged for 300 years, bring out the ideas of "unit operations" as being implicitly understood and show the organisation of transport of materials in the plant.

Chemists observing the process showed developing understanding of the chemistry of the operations and Wilson investigated the sequence of operations at plant level using chemical analyses. Chaptal developed the "synthetic" alum process as a projection of current chemical knowledge and Vauquelin's investigations could have led to fundamental changes in the raw materials used in Yorkshire.

Sulphuric acid and Gas Manufacture are sketched briefly. Both industries show the use of tests to evaluate raw materials and control the process; the involvement of chemists in fundamental research, as process innovations and carrying out investigations of the process at plant level; the development of processes based on chemical understanding and the development of works' techniques by non-chemists who could be considered embryo chemical engineers.

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INTRODUCTION

OBJECTS

The purpose of this enquiry is to examine the operation of industrial plants of the eighteenth and nineteenth century in which chemical processes were utilised in obtaining the end product or in monitoring its production. In particular, the process operations, their development, the development of plant itself, the process control and its development are investigated and outlined.

Immediately, one is faced with the problem of limiting the scope of investigation, since the field above is vast. Initially, it appeared that a "time scale" would be a suitable limitation. One could, for example, treat on certain chemical industries in the early nineteenth century or the late eighteenth century; however, the developments in different industries do not seem to fit into the same time scale. Another way of treating the time scale would be to regard the revolutionary changes in chemical thought of Lavoisier et al. as providing a date which would be a suitable natural break. For Britain one would suggest that the year 1790¹ when Lavoisier's "Elements" were translated into English could represent such a date. Many of the publications that seem designed to influence the industries described or consider their new tendencies fall into the "new" era. Furthermore, much of this work when of French origin, seems related to the new post-revolutionary Government initiative in France where the direct application of science to industrial projects was regarded as a noble aim and was organised to achieve definite ends. (2)

The "Industrial Investigation" work of Berthollet on dyeing (3) and of Pajot de Charmes on bleaching (4) and Chaptal in his "Chemistry applied to the Arts and Manufacture" (5) span the turn of the century. On the smaller scale, Clements and Desormes' paper on manufacture of sulphuric acid (6) and Henry's papers on salt (7) and illuminating gas (8) present good early 19th century examples of research in the chemical nature of industrial processes.

Yet, there is no general evidence that this era was a "take off" point for the chemical industry as a whole. Watson⁹ for example, writing in 1854, claimed

that there had been little change in alum making in ~~300~~ years. It would seem reasonable, therefore, to argue that each industry must be taken in its context and to consider some of the many other factors which could be used to explain the development in an industry. (see below page 16)

The next limitation to be faced is in the selection of industries which can be analysed according to the breakdown given in the first paragraph. What in any case is the chemical industry? Hardie and Davidson Pratt (10) describe it as "matter transforming industry" which produces chemical or physical changes in the nature of substances." They go on to point out that such a definition can "obscure the actual scope of chemical technology" and that, therefore, the usual title is "Chemical and Allied Industries" - where chemical industries produce named and recognisable "pure substances" and the allied industries produce the "mixtures" such as gas, glass and soap. It is this latter concept which will be used here.

This definition is taken to exclude the ferrous metal industries from "allied industries" yet the industry could easily be described in terms of the criteria mentioned in the first paragraph. In particular, as early as 1722, Reaumur was describing the use of visual observation of the crystal structure revealed in the metal fracture surface as a guideline in the determining of its suitability in steel making (see also plate 1).

Nonetheless, it has been found convenient to investigate the three dissimilar industries of Alum, Coal Gas and Sulphuric Acid manufacture in this enquiry and each in their own way can be examined according to the criteria mentioned above.

The Alum industry described below is pre-Spence and the description relies on both contemporary and later accounts but especially on manuscript material. In the case of sulphuric acid, the account is based on printed material, both contemporary and modern, and describes the lead chamber process. The survey of coal gas manufacture relies mainly on contemporary accounts.

pl. 6. pag. 200.

fig. 1.

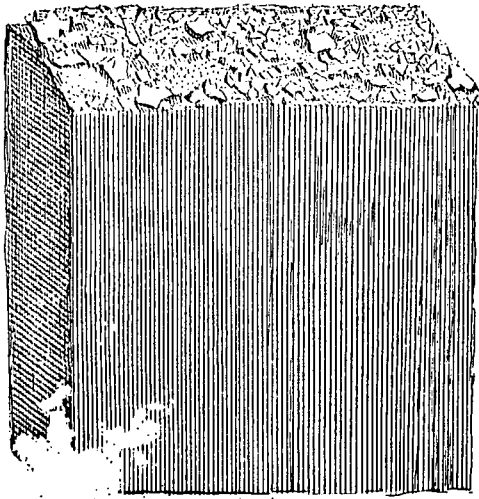


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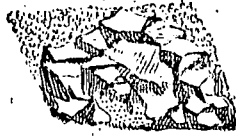


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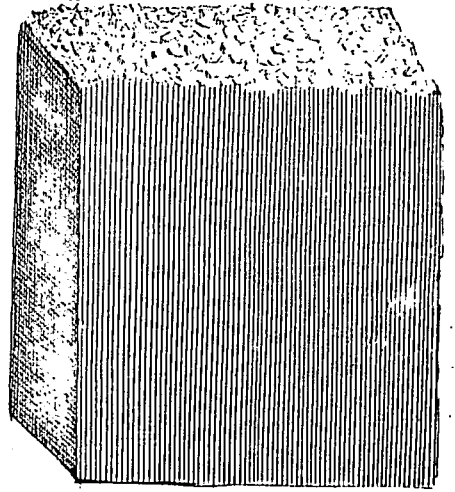


fig. 4.



fig. 7.



fig. 8.



fig. 5.

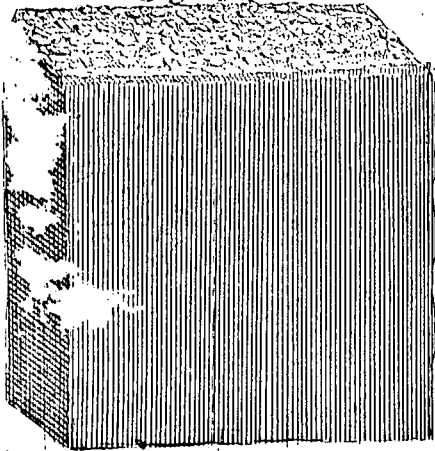


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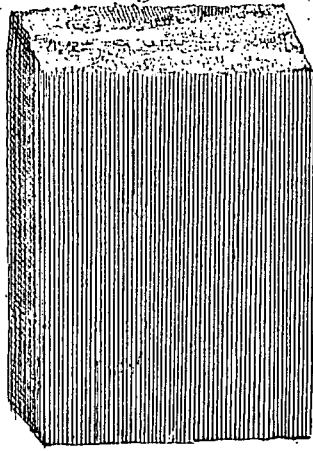


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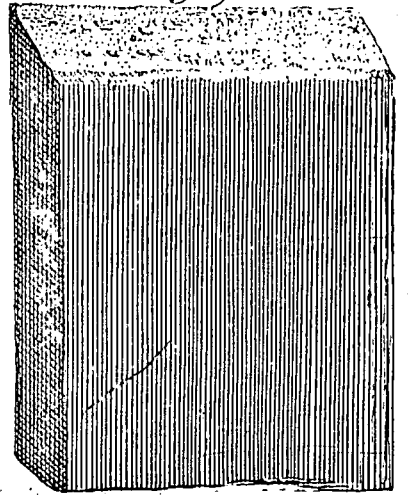


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fig. 14.



fig. 11.

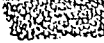


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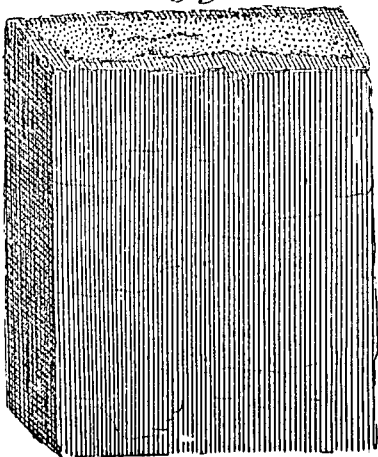


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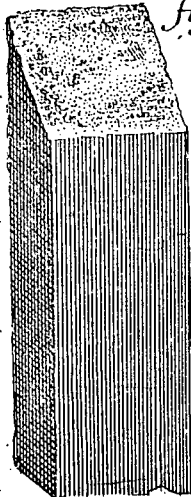


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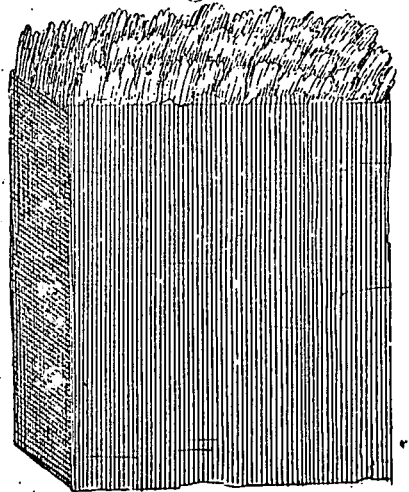


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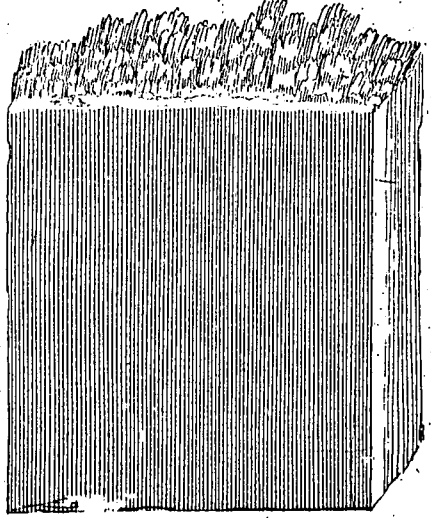


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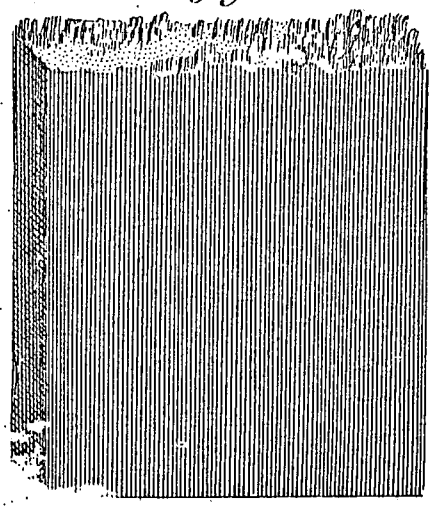


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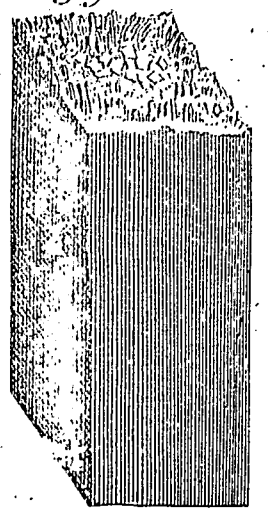


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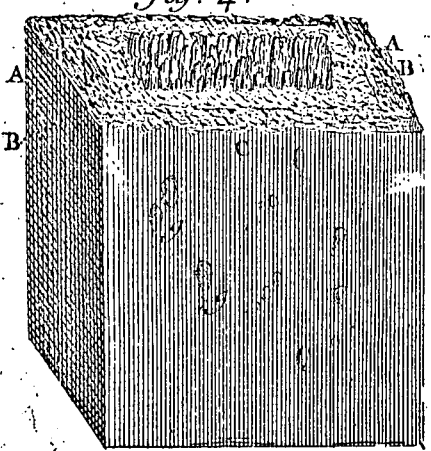


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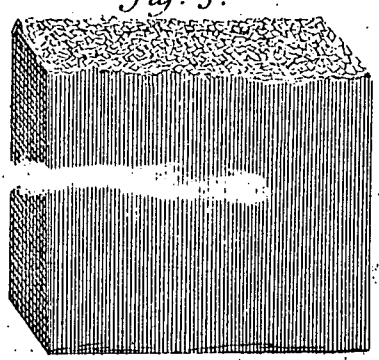
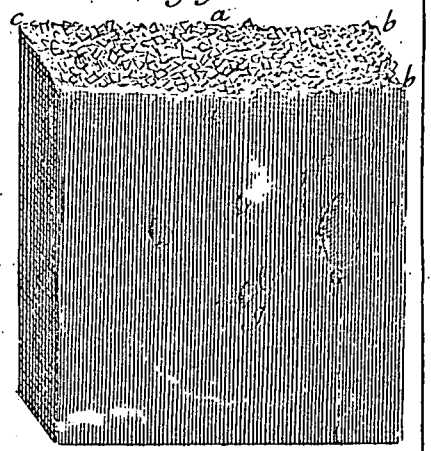


fig. 6.



o. fig. 7.

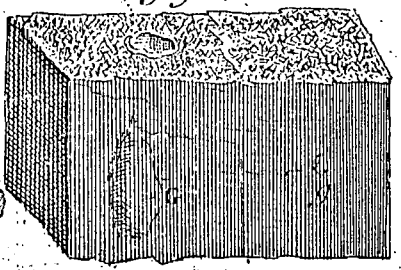


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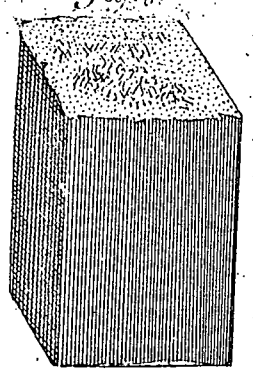


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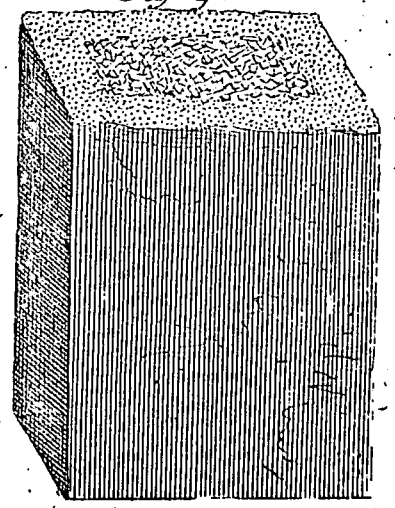
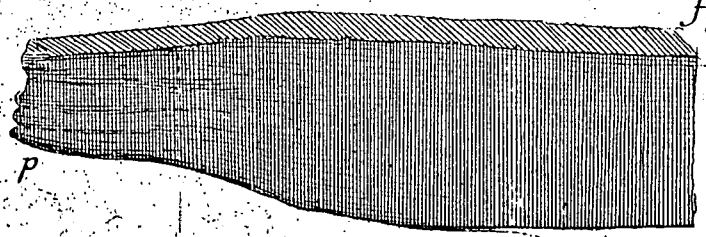


fig. 10.



Due to the different nature of the sources, the accounts differ considerably in detail. It is possible, and valuable, in the case of alum manufacture to place the ~~industry~~ into the geographical setting of North Yorkshire where, for example, the manuscript evidence can be used to show the details of management of a plant with details of raw material sources and input, methods of work and payment, the distribution of products and details of the process, control and development.

In the cases of the gas and sulphuric acid, the accounts are more general in the sense that they are not based on manuscript records of managers. Although it could be argued that Accum's treatises are specific to the Gas Light Company's early operations, they are not in fact so designed and must be thought of as texts on the production of gas.

In no way can these accounts be considered ^{complete,} in fact the aims of the first paragraph are themselves limited. We are not concerned - except in so far as it affected plant - with demands for the products or the general economic scene in which they fit.¹² The economics of raw material supply is of concern only in so far as it is a factor leading to process development.¹³ The sale of the product is of interest here only where there is some evidence of quality control or examination by the purchasers (see Note 285a) We are not concerned with the essential engineering services required on the plant although engineering maintenance on all these plants would be a major concern of their managers and this is to some extent mentioned in the account but only where it affects design or construction as for example to indicate how lead sheets could be joined (14) and how gas pressures could be maintained. (15) The alum account contains more detail than the others for the reasons described above.

The relationship between science and technology in the eighteenth and nineteenth century as a general issue is also far too vast to be considered in detail in this account but it must be reviewed in brief.

THE RELATIONSHIP BETWEEN SCIENCE AND INDUSTRY.

Solla Price posed the question in its opposite form "Is technology historically independent of science" (16) and saw significance in the amount of published contemporary material on a technological topic as showing the degree of development taking place in the field of technology.

There is no attempt in this approach to find evidence which shows in any individual case relationship between industry (technology) and science.

Certainly, the accounts of these historians tend to fit into one of three categories.

The historians of chemistry sometimes include a reference to industrial activity but usually that of the nineteenth century. Multhauf (17) is exceptional in considering the seventeenth century. Often, industry is not considered.

Historians of chemical industry such as Clow,¹⁸ Musson and Robinson and Taylor¹⁹ often take cognisance of theory and Musson and Robinson and Clow in particular go to some trouble to relate chemistry to industrial development as in the development of chlorine bleaching by Black and Watt on behalf of Watt's father-in-law (21) or by Milne in Aberdeen (22) or conversely by Henry in Manchester (23) - the dispute arising as to the first in development.

Industrial historians where authors investigate the individual commercial concern of industry are a more recent development and usually reported as Industrial Archeology. (24) Chemical technology has not been a major concern in the past of such works but useful articles are now appearing.²⁵

The difficulty is to relate chemical theory to industrial practice. Often, authors of the first two categories separate developments in chemistry and industry whilst mentioning that the two occur contemporaneously. This occurs in the History of Technology, volume IV chapter 8 where Holmyard describes the development of chemical theory and Clow separately describes the course of chemical production. (26)

On the other hand, the value of science to industry was almost axiomatic

in the eighteenth century and sometimes earlier.

Réaumur was indefatigable in demonstrating this (28) and it may appear from the second paragraph of this introduction that I presuppose that the savants influenced the industrial practice of the day. Indeed in Chaptal, one may find many direct relationships of the type where

1. "A chemist using a known process, developed, or had developed, a plant to produce a standardised product."

Although often in the case he mentions, Chaptal is the chemist concerned (29) Other examples are William Losh (see page 66) and Roebuck (see page 118).

Alternatively can we find situations where

11. "A chemist is called in by an industrial concern to advise as consultant and devise a realistic course of action to improve production or to rationalise it."

The example of chlorine bleaching given above seems to answer the criterion as does the work of Higgins on Rum Manufacture (30), Black on quality of Kelp (31) and Faraday on Alum manufacture. (32)

Similarly, we can find examples where

111. "An Employee not necessarily a qualified chemist is employed to investigate the process experimentally and in situ or is required to carry out control tests of a chemical nature on the intermediate 'products' in the process."

Here we may note the position of the unknown person who undertook laboratory investigations at Loftus Alum Works in 1805 (33) together with the known Alexander Tod who carried out such investigations in 1830 (34) and of course the often unnamed liquormen who used density tests to evaluate their liquors (35).

Far more difficult a question to answer is this? "Was the chemical industry organised in a scientific manner?" - and here we look for the relationship.

- IV. "A manager organises his plant so that the flow of materials and energy is monitored by workmen who carry out clear functions and who may use clear tests with known results to monitor the intermediate products so as to obtain the best yields of a recognised quality."

To obtain a satisfactory answer to these latter questions, we do not need to find academically qualified chemists operating or advising at plant level.

However, since we may not find such personnel, it is important to see what scientific principles were in use, because these ideas are often not expressed in any explicit manner.

The latter two relationships may seem to be the most useful in evaluating industrial development and a study of the Alum manufacture in my belief brings out sustained examples of both. (36) Thus, this manufacture could be called scientifically organised and has been described by academic writers as though it were so,³⁷ although no qualified chemist had participated directly in its early organisation.

The managers often took the opposite or anti-academic position as when George Dodds, the manager of Bowby alum works wrote to one of the partners on March 3rd 1786. (38)

"(I can now tell you) that Sir Thomas Dundas is for putting his Scheme in execution which I named to you last Autumn, but the Work is not to be stopped. A new House is to be built [and] the Works enlarged to ^{draw} 18 pans - the process is to be entirely altered and a person at present is learning to make Alum with Dr. Black of Edinburgh - what will come of this romantick Scheme, I do not know, but it will probably now [be] tried if Chemical Skill will make an improvement in that very nice and essential point of our business - the art of mixing and managing our ingredients so as to crystallise and form Alum". (reproduced as page 9)

Sir Thomas was interested in the success of the family alum works and we find him writing to his father about the state of the alum houses. (39) Certainly this interest raised ribald comment from nearby works as when Dodds, again writing to his employer, remarked that, at Loftus, they now had five alum makers with Sir Thomas making a sixth. (40)

Such reaction could be called narrow minded and equally it could be considered the normal reaction of the "professional" manager who resented interference with the organising of his plant. The Loftus manager must have felt this as Dodds reported that

"Farquarson, Sir Thos's Agent at the Works, though a drunken and disagreeable person, in many respects - 'tis much I think to his Credit - opposed this Scheme - which has not a little exasperated Sir Thomas, against him so that Sir Thos has been enquiring for another but I suppose this will blow over and they will not part." (41)

In fact, Farquharson, who was noted for this type of reaction, ceased to be Agent at some point between this letter being written and the year 1788 when Thomas Napper became Agent, (42) Although there is no evidence that this led to any immediate developments in the Loftus alum manufacturing process.

EMPIRICISM

It could be argued that the relationships 111 & 1V describe an empirical approach to organising a chemical plant and both Clow (43) and Taylor⁴⁴ believed that the eighteenth century was an empirical era in chemistry and that this acted as a limiting factor.

Taylor expressed it thus

"... the chemical industries and crafts that flourished up to and during the eighteenth century were almost entirely empirical ... the chemistry of the time did not afford them any indication or method by which they might improve their processes or devise new ones." (45)

and goes on to say that this situation had changed drastically by the middle of the nineteenth century when the

"... majority of industrial processes ... could be given an explanation in terms of chemical reaction ... (which) ... enabled the manufacturer to devise new ways of attaining their ends." (46)

Gibbs takes the contrasting view that

"(by the first half of the eighteenth century) the point had been reached where science and particularly chemistry could begin to give a lead to several manufacturers." (47)

Daumas goes further, differentiating between the industrial development towards large scale units in the eighteenth century and the contemporary development in science towards the latter end of the eighteenth century -

Lavoisier's revolution in chemistry. He argues that

"The (large scale) chemical industry... developed during a period that has long been regarded as unimportant. The fame of the work of Lavoisier and the chemists of his generation led to the belief that until then, chemistry did not exist. The historians of science have now recognised this error. But they have continued to believe that the major chemical industries were born spontaneously at the beginning of the nineteenth century." (48)

Much of Daumas' quoted evidence is derived from Diderot's Encyclopedia (49) and other such examples have already been quoted above.

Gillispie also claims that the French encyclopedic ventures of the mid eighteenth century were

"attempts to lift the arts and trades out of the slough of ignorant tradition and by rational description and classification to find them their rightful place within the great unity of human knowledge. (51)

The outlook of Gillispie is that

"when scientists turned to industry, it was to classify the trades, to study the processes and to classify the principles. In this ~~taxonomic~~ fashion, science was indeed applied to industry and very widely." (52)

The industries quoted in support of this position were mainly French and it was remarked that by the end of the eighteenth century, most of the major French chemical plants were managed by men of scientific background (53) and hence, it was argued that the main manner in which science was applied to industry was in the application of scientifically educated personnel to industrial problems. The era quoted is post Lavoisier and examples of this phenomenon are given above and may also be sought in the pages of "Annales de Chimie" 1789-1815. (54)

Earlier examples are mentioned above and in particular, Chisholm is worthy of notice as an assistant to Lewis (55) who applied simple titrimetric techniques to problems of industrial interest - Rancke Madsen (56) mentioned these and other early analytical controls using titrimetry. Wedgewood later employed Chisholm and Schofield indicates that it was to assist in Wedgewood's industrial research. (57)

Were scientists or science applied to industry or did they describe an essentially empirical development? As Musson remarks (58) "much of the debate hinges on what interpretations are given to the words science and empiricism or to pure and applied science." He believes too strong a distinction may be made between these concepts and that in practice the distinction between them is often blurred.

Empiricism is in any case a much maligned concept. It is still with us as can be seen from a glance at the British standards tests in almost any

branch of chemical and allied industries (59) or in the development of plant^t at pilot plant stage where one is ^striving to obtain optimum results. (60)

A sense of wonder is aroused therefore at the happy assurance that the limiting factors in process development in the eighteenth century could be more easily overcome after the chemical revolution - or as it is more usually put - that empirical methods alone were restricted in what they could achieve before the "Chemical Revolution" of the late eighteenth century.

It seems to me more likely that the eighteenth century industrialist was more concerned with profitability and cost effectiveness than with technical development as such. If development obviously improved profitability, it was acceptable, but risking capital to prove the advantage of development had unhappy precedents in both Roebuck in his operations at Carron Iron Company (61), especially his involvement with James Watt and the early steam engine and Lord Dundonald's ill-fated operations on many fronts. (62)

ORIGINS OF THE CHEMICAL ENGINEER.

It may appear that the question of science related to industry and in particular chemistry related to chemical and allied industries is not the most important relationship to be pursued. Today, we regard the design and organisation of a chemical plant as the province of the chemical engineer, although chemists may be involved in research or development and ultimately in control of the process. Is there any evidence that the early plant managers were in any sense chemical engineers in embryo? This term seems first to appear around the decade of the 1870's⁶³ when certain individuals so described themselves (see plate 2) I feel we are here looking for positive examples of the fourth relationship above.

What sort of organisations are we looking for in such plants?

(a) identification of the process as composed of separate unit operations which could be regarded as general operations not specific to the particular process on that plant. Such operations might include evaporation, crystallisation, solution, recrystallisation, distillation and filtration. the design

FRONTISPIECE.

A

PRACTICAL TREATISE

ON THE

MANUFACTURE OF

SULPHURIC ACID.

BY

ALFRED G. LOCK AND CHARLES G. LOCK,

CONSULTING CHEMICAL ENGINEERS.

5522



*With 77 Construction Plates, drawn to Scale Measurements,
and other Illustrations.*



London:

SAMPSON LOW, MARSTON, SEARLE, AND RIVINGTON,

CROWN BUILDINGS, 188, FLEET STREET.

1879.

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of the reaction vessels to achieve better conditions for the reaction can be included here. Where an improvement in any of these operations is found, especially where the improvement is seen as a utilisation of basic physical principles, it gives credence to the idea that the particular operation was regarded implicitly as a "unit operation" and this concept is found in dictionaries such as those of Ure and Knapp who also relate different industries through them. (64) It would be useful to know whether developments in unit operation^s were developed in situ or transmitted through an industry or even from industry to industry. There is some evidence that in the case of development of furnaces (65) and stills (66) that this took place as a separate art and the utilisation of waste heat has been traced from the seventeenth century. (67)

(b) That the transport and flow of materials was organised efficiently and preferably using methods other than men with barrows or, in other words, was there any signs of the development of continuous operation of plant^t. This could be described as seeking a material balance for the different parts of the plant and at the embryonic stage this could be considered achieved if the plant could operate smoothly without stockpiles or shortage arising at some intermediate stage in the process. (68) The waste of energy⁶⁹ in plants is today still immense, although this is now always due to the inability to conserve it, but more the negative economic motivation in so doing.

(c) We could also seek to find process development in for example the replacement of raw materials by improved sources (70) by reorganising plant and operational duties to achieve a greater yield improved product and/or the re-cycling or better utilisation of waste material (71).

However, to obtain the results in (c) above, we need to exert some monitoring of materials, in order to ascertain whether the aims have been achieved and, here again, we are looking for the emergence in embryo of another member of the modern plant team.

ORIGINS OF THE WORKS CHEMIST

The control of the process, testing of raw material and finished products

and "trouble shooting" investigations often falls to the lot of the works chemist. The control, ⁷² or monitoring function could be split as follows:-

- a) monitoring the constancy of raw materials often including water.
- b) monitoring the constancy of intermediate products as a check ^{of} their suitability for the next operation or often in batch production, to determine the quantities for mixing in the subsequent operation.
- c) monitoring constancy of product.

These controls could be carried out by trusted operators and thus a delegation of duties could be effected. In any case, other controls such as control ^{of} flow of materials, or temperature and pressure controls, ⁷³ would ^{not} obviously be the Works Chemist's task, but that of management or delegated operatives.

Nevertheless, if we can find an operative trusted with these duties, or some of them, it appears we are finding a works chemist in embryo.

The third relation above seems to embody the work of the works chemist and as we shall see in the alum accounts, early examples of plant laboratories (74) and the existence of both monitoring and development investigations (75) can be found in the Loftus works. Density monitoring of intermediates appears to date back to 1612 (76).

Of course the embryo chemical engineer and works chemist could be the same person in any plant and in the case of Chaptal and Parkes (77) we may find that these are in addition examples of the first relationship above which we could now describe as development chemists or chemical entrepreneurs.

It seems, however, that the consulting chemist has been always an academic chemist called in by the manufacturer and his function is of, course, that outlined in the second relationship above. (78)

PARALLELS.

The concepts of plant development (or process development) and process control have been described in the previous two sections. The discussion indicates that their development may also be associated with the creation of

recognisable professions and so this development may contribute to the professionalisation of science and technology.⁷⁹ (see conclusion page 151 below)

In this enquiry, then, we are concerned more with the scientific nature of the tasks performed by industrial personnel than with the inter-relation of science and technology. However, the involvement of scientists is apparent in both gas and sulphuric acid manufacture especially in consultancy~~ing~~ but also in development. (80)

Other factors influencing development are treated in context but not extensively. For example, the development in chemical industry was affected by economic forces of the time and one could mention the price of kelp (81) and the lack of initial demand for vast amounts of sulphuric acid : (82) political forces - the wars with France and their effect on trade: (83) the operation of the patents law - both in its effect (84) and its breach (85) which led to secrecy concerning operations (86) both of these effects can be seen in the gas and sulphuric acid industries : the lack of communications - although alum and sulphuric acid had better communications than might be expected (87) and of course the operation of price cartels which also controlled production but which in the case of alum do not appear to have had a great effect on the development of the process.(88)

THE ALUM INDUSTRY.

The alums are a series of sulphates or chromates containing both monovalent and tervalent ions in the crystal lattice in almost equal numbers.

A general formula would be $M^1, M^2(SO_4)_2 \cdot 12H_2O$ although many may feel happier with $(M^1)_2SO_4 \cdot (M^2)_2(SO_4)_3 \cdot 24H_2O$.

M^1 , the monovalent metal ion could be potassium, sodium, ammonium - to take the ions most involved in practice. It could also be a mixture of any two or more monovalent ions and the commercial alum was often a mixed Potassium/ammonium alum.

The Alums are distinctive in that they crystallise in the same octahedral crystal form. (For the importance of this in "quality control" see below *note 285a*)

Commercial alums were used in medicine, fireproofing and extensively in the dyeing industry to make "lakes" and as mordants.

Manufacture of Alum.

1. Introduction.

The purpose of this section is to trace the development of the English processes in use in North Yorkshire from the seventeenth century to their demise in the second half of the nineteenth century. The Scottish process at Hurlet and Campsie, which commenced about the end of the eighteenth century and was wound up at the end of the nineteenth century, is similar in basis and also described. The process of Spence, which supplanted the traditional process, is also traced briefly, from its (possible) origin.

The use of the term "English process" could be criticised since it was also for part of the period under discussion in use in Scotland and also in Germany, however, the Whitby process predates the Scottish and German process seems similar to the Scottish. Turton, in his "Alum Farm" reviews the early history of the industry and points to its continental antecedents. Singer also brings this up in his history of the "Earliest Chemical Industry." However, the term "English process" is suitable in its context since the purpose here is to trace the development of the process and practice in use in North Yorkshire

by observations of that practice by various individuals and at varying times during the period it was in use.

Details of the extent of the industry are brought together in the section entitled "The Account of the Participant" which is drawn from the manuscripts of the Agents and Managers who operated the plants from mid-eighteenth century into the nineteenth century.

It might be asked why, when such material is at hand, it is necessary to use the accounts of non-participants and compilers of dictionaries.

Apart from the evident argument, that seeing a process through many pairs of eyes is preferable to one man's view, we need the views of dictionaries for two main reasons.

(1) By compiling and rationalising they "ordered" the process and separated it into sub processes, which are occasionally identical with the unit operations of the modern chemical engineer (see Ure's account below and the earlier Chaptal model.)

This "structuring" is needed to comprehend the extremely varied and detailed manuscripts whose authors did not need to remind themselves of their proprietors of the overall process and rarely gave an account of even part of the process.

(2) The compiler of a chemical dictionary, writing for a literate and critical audience, reassessed the process in terms of the chemistry of the day and provided a cumulative view of the chemical understanding of the process and the chemical control thereof.

Using selected accounts of the process by, in general, well-known authors of their era, we can trace the extent to which the process had developed although its basic structure remained unchanged. (92)

The degree of the author's appreciation of the process is also tested, since at the expense of some repetition of some details in the different accounts, one can note whether the authors were giving due weight to the technical management of materials, particularly transport of materials and use of energy

in the plant.

As far as possible, repetition of details common to all the accounts is avoided although it may be necessary to note the absence of details in some accounts and certain points must be included to preserve continuity of the narrative.

By keeping the accounts physically separate, the problem of preserving chronology in a general account is avoided but the system makes comparison and evaluation difficult to embody in the text and these are usually included as a conclusion and in linking one account with the next.

2. SEVENTEENTH CENTURY PROCESS.

The early plants in North Yorkshire began production in the seventeenth century although three had been in operation before 1600. The plants, their duration and location will be dealt with in more detail below.

A description of the seventeenth century mode of operation was presented in 1678 to the Royal Society by Daniel Colwall (?-1690), an active member of the Royal Society since his election in 1663, whose generous financial support was of great use to them but whose contributions to the philosophical transactions were unimportant. ⁹³ This casual dismissal does not appear justified when one considers his reports on alum and copperas. His report on alum ⁹⁴ which follows appears very close to plant practice when compared to the managers manuscript.

1. Colwall's account of 1678 on the Whitby alum.

The alum shale is found under a "Cap of earth" which is removed. The shale is excavated and once exposed to the air "will moulder in pieces" or decompose rapidly; "as long as it continues in the earth or in water it remains hard stone." The excavated rock is now called Mine, and assembled for roasting.

The baring and clearing was carried out by day wage and pieceworkers and cost 1d - 2d a yard. ⁹⁵ The Mine was dug and broken into small pieces and barrowed to the heaps by the same operatives, this would cost 2d - 4d. ⁹⁶ The Mine is calcined with cinders of Newcastle coal, woods and furzes. The fire is made two feet and a half thick, two yards broad and ten yards long. Between each fire are stops made with wet rubbish, so that any one or more of them may be kindled without prejudice to the rest."

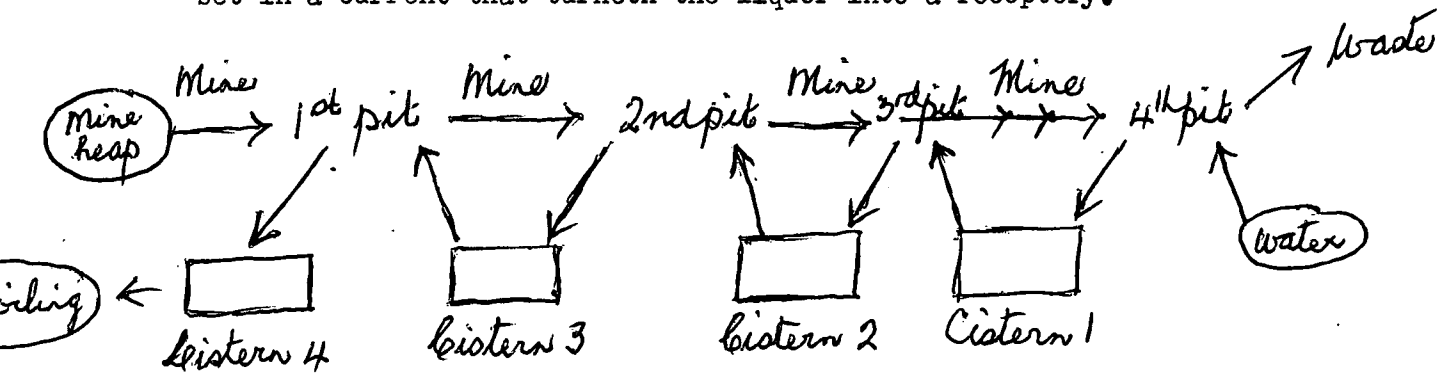
These "divisions of the heap" are not so clearly noted by subsequent authorities - except those in manuscripts - who give global dimensions. The fuel bed is covered with 8 - 10 yards of 'broken mine', the fires lit and more mine put on as the fire begins to consume the heap. The heap can be built to a height of 20 yards without any more fuel being added and it will continue to burn "stronger than at the first kindling so long as any sulphur remains in the stones."

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Turton reports the purchase of a calcining grate at 30s which with a weight of 3 cwts could support many small heaps. Insufficient or excessive burning causes the calcined mine to be black or red respectively.

"but where the fire passeth softly and of its own accord, it leaves the mine white which yields the best and greatest quantity of liquor. The mine thus calcined is put into pits of water, supported with frames of wood and rammed on all sides with clay."(98)

The oldest pits, according to a survey of 1625,⁹⁹ were wood and out of repair. These pits have the dimensions 10 yards X 5 yards X 5 feet and are connected by a channel to the cistern, or, as Colwall picturesquely puts it, "set in a current that turneth the liquor into a receptory."¹⁰⁰



Colwall puts it thus ... " Every pit of liquor, before it comes to boiling, is pumped into four separate pits of mine and every pit of mine is steeped in four separate liquors before it be thrown away, the last being always fresh mine."¹⁰¹

The diagram is, of course, schematic since by suitable pumping arrangements it may not be necessary to transfer both solid and liquid - although the 'turning' of the mine in transfer may have been considered beneficial.

Each steeping was of 14 hours duration so that the whole process took 4 days and the progressive concentration is, in the units of manufactures, two pounds, five pounds, eight pounds and twelve pounds. No interpretation is given but Singer¹⁰² states that these represent pounds excess weight over and above 100 lbs of water, which is 10 galls. If this is correct, then the progressive increase in specific gravity are from 1.02 through 1.05, 1.08 to 1.12 (assuming of course that the spring water supplied to the pits is almost free from dissolved solids - although of course, even if the original density of the water is greater than

unity, the progressive increase will be much the same. However, here is a clear indication of relating density and concentration.

The final liquor is run off directly into the "Boiling pans" which are of dimensions 9 ft X 5 ft X 2 $\frac{1}{2}$ ft set upon 2 $\frac{1}{2}$ " thick iron plates. These must have required continuous maintenanceⁿ by site craftsmen since Colwall remarks that the "pans are commonly new cast and the plates repaired five times in two years."

On an operating plant the boilers are filled two thirds full with "the liquor that comes from the alum or wherein the alum shoots which they call mothers," (103) these are respectively wash liquor or liquor from the crystallising operations. The other third is fresh liquor (or as its also called in the article "green liquor"). "Being thus filled with cold liquor, the fires having never been drawn out, it will boil again in less than two hours time."

If the fires are burningⁿ continuously over more than 24 hours, as this seems to indicate, and also if the pans were regularly recast, there must have been standby facilities i.e. extra pans and furnace space to take up the slack during maintenance and re-erection of the pans taken out of the line.

The liquor would boil down four inches in two hours and be replenished. After 24 hours, it would be expected to have a weight of thirty six pounds (104) or, using the comparison techniques above, a gravity^{of} 1.36. In appearance the liquor should "be greasy as it were, at the top; if nitrous, it will be thick, muddy and red." (105)

A hogshead of Kelp lees with a weight of 2 pennyweights is now added. This is explained at the end of the account "the liquors are measured by the Troyweight. So that half a pint of liquor (in latter accounts one third of a pint is the standard) must weight more than so much water by so many pennyweights. The use of the pennyweight is found in the time of Dr. Edward Jordan, born 1569 awarded M.D. Padua who was associated with alum making in 1614 and could have invented^{the} assay glass." (106)

On this basis, the specific gravity of the kelp can be calculated as 1.017.

Another unit is quoted earlier when Colwall speaks of the preparation of the Kelp lees which "are drawn off at two pound weight or thereabouts". This would, on Singer's hypothesis, give a specific gravity of 1.02. The difference between these two densities in the total mass of dissolved solids in a hogshead of 52.5 gallons amounts to a mass difference of 1.58 lbs which as we shall see below (107) is negligible.

The effect of this addition is to reduce the weight to 27 pounds weight (or specific gravity of 1.27) and the addition can also be monitored by inspection thus:-

"If the liquor is good, as soon as the lees of kelp are put into the boiler, they will work like yeast put to beer. But if the liquor in the boiler be nitrous, the kelp lees will stir in but very little and in this case the workmen must put in the more and stronger lees."

The reaction mixture is then run into a settler "as big as the boiler, made of lead, in which it stands about two hours, in which time all the nitre (108) and slum sink to the bottom."

The liquor is transferred to a wooden cooler, leaving the sediment behind, and 20 gallons of urine added and "if the liquor be red and consequentially nitrous, the more urine is required."

The provision of urine was a local industry and Colwall assumes (or he is informed) that it is of human origin since he piously remarks that "it is observed that the best urine is that which comes from poor labouring people who drink little strong drink." (109)

His comment on the control test does not however extol their honesty - he explains the need for the test.

"Because the country people who furnish the work with urine, do sometimes mingle it with sea water which cannot be discovered by weight, they try it by putting it to some of the boiling liquor. For so if the urine be good, it will work like yeast put to beer or ale, but if mingled, it will stir not more than so much water."

The liquors are left in the cooler for four days in temperate weather - the alum starts to crystallise (strikes) on the second day - and in hot weather an extra day is needed, but the liquor must not be left too long "otherwise it would,

as they say turn to Copperas, "and in cold weather this often happenēd as a matter of course.

"In frosty weather the cold strikes the alum too soon, not giving time for the nitre and slam to sink to the bottom, whereby they are mingled with the alum. This produceth double the quantity: but being foul is consumed in the washing."

At the end of the crystallising operation

"... that called mothers is scooped into a cistern, the alum remaining on the sides (and at the bottom: and from thence the mothers are pumped into the boiler again, so that every five days the liquor is boyled again, until it evaporates or turns into alum or slam."

Slam has been described as the "slimy" material deposited in the settler after concentration (but see the fuller discussion below on page 98)

The alum can now be removed from the cooler.

"put into a cistern and washed with water that hath been used for the same purpose, being about twelve pounds weight (e.g. 1.12)"

When concentrated this washing 'liquor' will be recycled to the boiler as indicated above. The recrystallisation or roaching is the final process.

"... it is put into another pan with a quantity of water where it melts and boils a little. Then it is scooped into a great cask, where it commonly stands ten days, and is then fit to take down to the market."

No mention is made of breaking or draining the cask or that the liquor would be suitable for a further boiling.

Because of Colwalls' direct and expressive use of language, this account has set out to use his words with minimum explanation and elucidation but the archaic style and vocabulary should not make us treat this account lightly

On the whole, the account is down to earth description. Although no mention of chemical understanding is made, control techniques are described throughout especially the following.

1. colour of the mine-heap to determine effectiveness of calcination
2. density tests on all solutions.
3. visual check on quantity of kelp required "effervescence"
4. titrimetric method for ammonia in urine.

Colwall mentions the existence of works near Preston in Lancashire but these are mentioned by most of the authors without any major description of them so no attempt will be made to include them in this narrative. Their

duration is however similar to the works we are describing.¹¹⁰

CHAPTAL'S "RATIONALISATION" OF ALUM MAKING.

Chaptal, writing in 1803,¹¹¹ used the new nomenclature devised by Lavoisier and Guyton de Morveau (and this was not his first ¹¹² important contribution to the alum manufacturing. ← a paper of 1789 is mentioned below), and this gives a very modern appearance to his account.

Jean Antoine Claude Chaptal (1756- 1832) was a chemical manufacturer, professor of chemistry at Montpellier and Minister of the Interior under Napoleon I who gave him the title of Comte de Chanteloup. He survived the demise of Napoleon and continued in public office.¹¹²

In his work "Chimie appliquee aux Arts", published in translation in England in 1807,¹¹³ Chaptal not only describes processes in use, but in many fields describes the process which he is using. Alum was one of the products he manufactured, but his own process, originally outlined in the paper of 1789,¹¹⁴ is a precursor of the Spence process which ultimately eclipsed the alum slate extraction and is discussed below. However, he also described the Whitby process among others.

Alum is described as ¹¹⁵ "triple salt ... a sulphate of alumina and potash;" of specific gravity 1.7 ; acid to litmus ; forming octahedral semi-transparent crystals which are soluble in 15 parts of water at 60°F and 0.75 parts of water at boiling point.

The process is split into three section:-

- A) Aluminization
- B) Lixiviation
- C) Crystallisation

1. Aluminization.

Chaptal explains that aluminium and sulphur are present in the rock but not combined and to effect this combination, the mineral could be left exposed to the atmosphere but due to the slowness of this method, heat is applied to the crushed mineral.

"It is in the proper regulation of these diffent^{er} agents, air, water and heat that the art of aluminization consists."

This is an unhelpful generalisation but when he mentions the Whitby example, he describes the preparation of a bed of "faggots" of 10' X 12' wide and the rock is piled on top, using a "scaffold", set up alongside, until the heap is about 50' long by 40' high and

"They do not wait until it is finished before lighting the fire, because as it penetrates the mass only slowly, it is necessary frequently to review it."

The size of the heap mentioned appears to correspond more to divisions of the heap mentioned by Colwall than the massive heaps of other authors and the problems of excessive firing of the heap are not mentioned.

2. Lixiviation.

The purpose is "to obtain the sulphate of alum separately."

The calcined shale is bathed in tanks "sunk in the ground in order to preserve as much as possible a uniformity of temperature."

Three banks of pits erected, the upper one with nearly exhausted ore,

"so that the water may gradually take up the different salts and acquire a degree of concentration amounted from 15 to 25 degrees according to Beaume's aerometer (116)" although he describes the Whitby process involving bathing the calcinate twice, each time standing for 24 hours, and using the second washing to leach the fresh mine. He also describes how one could varnish the walls of the pits with yellow wax and resin mixed with Spanish brown but as is described elsewhere the Yorkshire works made do with clay (see page 21).

In any case, the following practical considerations should be observed:

- a) the rock should be broken up to help the water to "penetrate more effectively" but not powdered.
- b) the calcined material is to have a "certain thickness" since the solution becomes more concentrated in proportion to the height of the stratum through which it percolates.
- c) "the water should cover the mineral by several inches."
- d) the water should be left until no further solution takes place.

This last suggestion seems to make nonsense of the gradual solution mentioned above since it implies leaving the water until it becomes saturated.

The liquor is run into stone cisterns and left to clarify "by the deposition of any extraneous matters".

3) Crystallisation

The liquors are boiled in lead 'cauldrons' of dimensions 10 to 12 feet by 7 to 8 feet by 2 to 3 feet. Mother liquors are added from a previous process and the pans stirred to prevent precipitation.

"...as they might injure the cauldrons by forming a crust which interposing between the fluid and the metal would expose this last to the direct action of the heat."

Chaptal then gives a list of alternatives for determining the point at which the correct concentration is reached.

- a) concentrate to 60°B (but in some works only 35°B)
- b) fresh eggs remaining afloat.
- c) weigh bottle of liquor and compare weight with pure water.
- d) Fill cup and check whether it crystallises on cooling.
- e) boil down until reaches marked level.

At the end of the day, due to the variable composition "experience alone can determine the proper point."

A brief glance at these methods will demonstrate that they include all the methods mentioned in the other accounts.

Alkali must be added to the liquor which is first removed from the pans. If iron (II) sulphate is present, this is crystallised out before adding the alkali which in England is kelp (quoting Jars.) He later mentions the use of "putrescent urine" as furnishing ammonia and he also indicates, surprisingly, soda as an alternative alkali.

Alums are often mixed, since in some manufactories both potash and urine are used.

He finally points out that the alum is not yet pure enough and needs to be recrystallised.

Chaptal's account is ordered and contributes something to the chemical understanding (see below page (68) of the process, but to fill in contemporary details, it is necessary to look at one or two local accounts of the North Yorkshire process.

Winter's Account of the Whitby Process dated 10th March 1810. ¹¹⁷

The Alum works around the Whitby area are almost invariably situated on the coast to facilitate disposal of the "immense quantity of refuse schistus and rubbish", (as the covering strata above the aluminous schistus are called) and also to save on land transport costs which would be incurred in excess of sea transport of coals from Sunderland and South Shields.

For these reasons, he suggests that the inland works have been reduced in number.

He describes the covering strata as being composed of alluvial soil, sandstone, ironstone shale and clay and goes on to describe the sandstone more fully, as a valuable building stone. Although this does not directly concern the process, it is dealt with below briefly when we consider the organisation of labour in baring the stone. (p.44)

The sandstone beds are between 4 yards and more than 50 yards thick.

Beneath these lie the alum shales which Winter has analysed at various depths. He concluded that as the depths increase, the sulphur content decreases and the bituminous content increases from which he assesses that 1 cubic yard of top shale is the equivalent of 5 cubic yards of "bottom" shale.

This scientifically based conclusion seems to be in direct contrast to the simple unqualified opposite statement of Colwall that

"The mine which lies deep in the earth and is indifferently well moistened with springs is the best. The dry mine is not good. And too much moisture cankers and corrupts the stone making it nitrous." ⁽¹¹⁸⁾

Winter gives the ultimate analysis of the stone's composition to be siliceous, alumina, magnesia, lime, oxide of iron, bitumen, sulphur and water. ¹¹⁹

The rubbish is first removed and the alum rock hewed out with "picks and javelins", then transported by a centre-wheeled barrow whose centre of gravity

is on the vertical line through the wheel hub. In this way, the full load of shale is supported by the wheel and the task of the workman is to keep it steady in transit. Winter assesses the capacity of the barrows at 10 barrows \equiv 1 solid yard. (this figure represents a full barrow, half and quarter barrows were also in use.) and give^s two cost factors.

1) distance to be transported; since the barrowmen are day wage workers (earning 2/6d per diem in winter and 3s. per diem in summer) and not paid by the number of barrows delivered on a weighted basis, therefore the longer the journey, the less is the output per manshift and the greater is the unit of expenditure.

2) ease of hewing depends mainly on the hardness of the rock (but also see page 20)

The barrowmen (see below) transport the rock to the site for roasting where a bed of fuel 4 yards by 2 yards high is prepared. The rock, which must be broken up, is poured on to the fuel bed and when a 4 feet covering is attained, the fires are kindled.

Other piles of wood are prepared beside the first one and the process repeated until the total heap can have dimensions of 150 feet and 200 feet at the base and 90 feet and 100 feet high.

Winter makes no mention of the breaks between the fires mentioned by Colwall above (p 20) and yet George Dodds, the Agent/Manager, of the Boulby Alum works mentioned by Winter in his account, writing to Mrs. Baker, one of the partners on October 2nd 1779 seems to indicate the continued use of the "stops of rubbish" when he says

"I now beging very much to doubt we shall not be able to keep ALL OUR FIRES in the winter, we have not a force of barrowmen at all competent to the consumption of burnt mine." (my emphasis.)

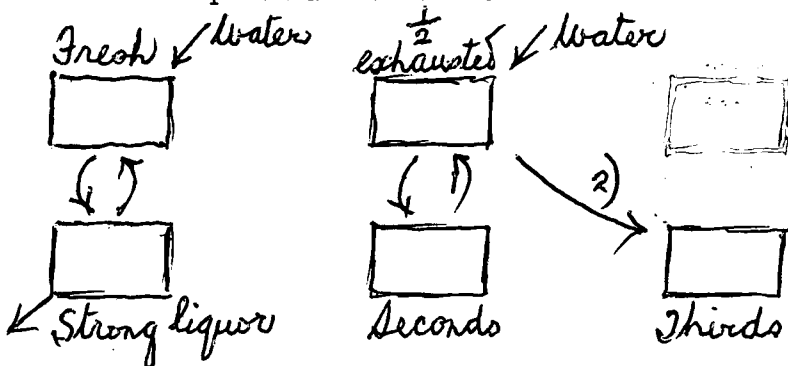
By the latter part of the statement, he is claiming that the heaps cannot be replenished as quickly as they burn through, due to shortage of labour.

Winter goes on to remark on the vast quantity of sulphurous acid gas lost to the air and the attempt (in his view) to prevent this by plastering the outside of the heap with wet ^{cl}shist. This, he claims, has little effect but keeps the wind out until it is eventually decomposed by rain.

The calcined shale is steeped in water in pits usually containing 60 cubic yards of impregnated water which is recycled to impregnate fresh mine until the specific gravity of the liquor is 1.15 or 12 pennyweight.

Winter does not mention Colwall's "Frames of Wood" on which the shale is laid. He further reckons that 130 tons of calcined shale give 1 ton of marketable alum.

The progress of the leaching can be summarized diagrammatically from this description as follows :-



the half exhausted mine is covered with water, successively, to take up the soluble salts and three grades of liquor are found in the pits - strong, seconds and thirds.

He seems not to have noticed the counter-current progress of the two streams of materials which Colwall has noticed over a century earlier. Winter's input is always fresh water and the only recycling is the use of strong liquor on new mine.

The strong liquor is now run to a cistern to deposit the lime and iron sulphate and the earth. In some works, the liquor is clarified by boiling and resettling in spite of the added expense of fuel.

This alum liquor is now transferred to the pans for boiling and from this point the observations should be somewhat different since the additional unit operation of preliminary settling has now been inserted in the flow.

The pans are of lead with dimensions length 10 feet, breadth, 4 feet 9 inches, ^{height} high at back 2 feet 2 inches, height at front 2 feet 8 inches. This innovation is to facilitate emptying the pans. The pans are made in situ in the alum house.

The mothers (does this mean only liquor from subsequent operations?) are pumped in each morning and topped up with fresh liquor (is this the green, or freshly made, liquor or is it a new batch of added material?) every two hours or as required.

The pans must be kept boiling and sedimentation thereby avoided lest "the pans (be) melted from the crust formed between the liquid and the lead."

Every morning, the concentrated liquor is run into a settler and alkaline lees of a specific gravity of 1.037 - 1.075 added. These lees "are leachings of kelp, black ashes or muriate of potash and the quantity required is determined as that required to reduce the specific gravity of the concentrated liquor to 1.35. (The specific gravity of the pan liquor has been previously determined and is sometimes as high as 1.45 to 1.5)

The mixture is allowed to stand for 2 hours then run off into a cooler.

If the specific gravity is less than or equal to 1.35, the liquor is left to crystallise; if greater than 1.35, urine is added to reduce the gravity to 1.35. The liquor is stirred and left.

"It must be observed that at a greater specific gravity than about 1.35, the liquor, instead of crystallising, would present us with a solid magma resembling grease."

After four days, the liquor is run back to the boiling pan and the crystals are dug out, washed in a tub, drained in a bin with holes and transferred to a pan.

"and as much water added as is found requisite to dissolve the whole of the alum when in the boiling state; the moment this is effected, the saturated boiling solution is run off into casks. These casks should stand about 16 days as they require that time to become perfectly cool in the summer season."

The casks are then dismantled and the "hollow casks of alum pierced and the 'tun liquor' which comes out is recycled to the pans. The outside of the alum is cleaned and the mass is then broken up and packed.

Winter's account has the advantage of being ~~clearly~~ written and excepting the differences mentioned above can be seen as expanding and bringing "up to date" Colwall's account. Furthermore, his account is supplemented by a local History of Whitby published there in 1817. The author, the Rev. Dr. George Woung acknowledges Winter, the plant Agents George Dodds and Mr. Bathgate and in addition claims to be in possession of papers on alum belonging to "the late Ephraim Jowsey, a noted alum maker."¹²³

It is from this account of Young that the more modern author Turton takes his description of the use of the alum bottle in density determination.

YOUNG'S ACCOUNT OF 1817. ~~121~~

Young notes that the ore is hewed from the top and "downwards in different floors or desses as they are called till the rock becomes too unproductive to be wrought any deeper." The explanation of the word "dess" is needed to comprehend the manuscripts.

The rest of the process is described as in Winter's account except that only muriate of potash is given as the alkali and Young comments that use of this alkali has only become general in the previous few years and gives an interesting time scale for the supplanting of one alkali for another for which he appears to be indebted to the Loftus proprietors. This time scale can be summarised as follows

Before 1789, kelp universal raw material

1789, black ashes (from soap boilers) and kelp

1794, kelp began to be entirely laid aside

1801, muriate of potash and black ashes and in two or three years, the muriate began to supercede the ashes.

From 1794, use of urine "fallen into disuse". *Information* far more important to the understanding of any of the working on alum is given when Young describes the method of measuring density used in alum works.

"A bottle ... containing about $\frac{1}{3}$ of a pint ... having a short neck ... is filled with distilled water or clear spring water ... put into one scale and a piece of lead is made exactly to balance it; this is called the counter-weight or water-weight. The bottle is emptied and dried ... counter-weight into one scale ... empty bottle into the other and small lead shot is poured in beside the latter till the scales are poised. The small lead shot, the weight of which exactly corresponds to that of the water which was in the bottle is called 80 pennyweights ... 80 pennyweights being equaliyent to 2.0 and 1 pennyweight to 1.0125."

He quotes Mr. Bathgate as having demonstrated that 50 tons of calcined rock will produce 1 ton of finished alum and in general gives production as 1 ton of alum from 120 - 130 tons calcinate.

Each hundred tons of alum produced requires 22 tons of muriate of potash, and following Winter, he notes that each pan gives 4 cwt of alum and consumes 18 bushels of coal in the heating of it.

The last sections give a clear picture of the different operations used in the manufacture of alum from alum shale and an early breakdown into "operations" is found in Chaptal.

They also indicate the problems of the observer who was not directly involved in the manufacture. His errors of description or of omission, especially the latter, may be due to the expectations he has in the general knowledge of his readers as much as lack of observation on his ^a part.

Although we shall be looking at the descriptions of other authors below (~~Ure and Knapp~~) mainly for their chemical understanding, we can now look directly at the accounts of those who managed the North Yorkshire works and we have used Ure's "~~unit~~ unit operations" (see page 77) to simplify and "order" the manuscript material

ACCOUNT OF THE PARTICIPANTS.

Sources.

This account relies mainly on two sets of manuscript material.

a) The Baker-Baker papers which are family records of the Baker family of Elamore Hall, situated between Murton and Hetton-le-Hole in the county of Durham. These manuscripts are kept in the Department of Palaeography and Diplomatic, University of Durham, and a separate volume catalogues the alum papers. These papers consist of correspondence especially of the agents, cost records, monthly reports, occasional memoranda and 'alum accounts' - all referring to Boulby Alum works.

b) The Zetland (Loftus) papers which are family records of the Dundas family (later Lord Dundas, Earl of Zetland etc.) whose interest^s stretched into Scotland and elsewhere. The family became associated with Loftus Hall in 1840. These records are kept in the North Yorkshire County Council Record Office, Northallerton, and some of the specific alum papers are catalogued separately but not in a separate volume. These items include day books, experiment books, letter books etc. However, much of the agents' correspondence is found under the correspondence records of the relevant member of the Dundas family. These

records refer to the Loftus Alum works, although the final letter from Towers to Westgarth instructing him to commence winding up Boulby is also in these records. Since there were a number of alum works on the North Yorkshire coast and inland, it would be useful to survey these briefly.

Operating Plant.

Dr. Young in 1817, lists 23 sites connected with alum manufacture in what he conjectures is the chronological order of their commencement.¹²⁵ He does not always give dates of commencement, and often refers to *theirs* having been in operation "20 years" (say) or having closed down "12 years ago" - or worse - were in production "more than ..." For this reason, in this abstract, any date calculated from these beguiling data is underlined. Any year not underlined is quoted directly from Young (a map copied from Young's "History" shows the location. (see page 37))

Site	Duration of Operation	Proprietors	Present Position (1817)	Final Closure
1. Belman Bank	1595 - <u>1620</u>		Closed	(1870)
2. Guisborough	1600 - 1620	Lord d'Arcy	Closed	
3. Sandsend	1615 -	(Lord Mulgarave)	"Prosper's"	(1867)
4. Old Peak	<u>1615</u> - <u>1618</u>		Closed	
5. Boulby	1615 -	(Baker & Jackson)	"Respectable works."	(1871)
6. Lofthouse	1615 -	(Dundas)	"Flourishing"	(1863)
7. Peak	<u>1615</u> -	Cooke (Maitland's)	"Operating"	(1862)
8. Saltwick	1649 - 1708 1755 - 1791	Chomley Cookson	Closed	
9. Littlebeck	<u>1660</u> - 1809	Jackson/Danby Ridley	Closed	
10. Carleton	1680 - 1774	Capt. Pressick	Closed	
11. Holmes	~ 1680 → ?		Closed	
12. Ashholme	~ 1680 → ?		Closed	
13. Rockhole	1680 - <u>1686</u>		Closed	
14. Selby Hagg	1680 - 1720 1765 - 1772	John Hall	Closed	
15. Hobb Wood	(remains of mine heap ; doubtful if alum made here)			
16. Kirby in Cleveland	- 1730		Closed	
17. Kettlewell	1728 - 1736 1742 - 1754 1767 -	Ambrose Newton Lord Mulgrave	Prosper's	(1871)

18. Osmotherly	1752 - 1772		Closed	
19. Stoupe Brow	1752 -	(Mallinsons)		(1817)
20. Eskdaleside	1764 -	J. Yeoman R. Jackson		(1818)
21. Godeland Banks	1765 - 1805	Scarth/Thornhill	Closed	
22. Ayton	1745 - 1771		Closed	
23. Guisborough	1766 - 1804		Closed	(see Note 9)

The final closure dates are those given in a very useful table on "Principal Alum Works"; Periods of Operation" in "Cleveland Industrial Archaeologist No. 2 (1975)"¹²⁶. That two works should be listed on closing in 1817, the year of Young's book is probably due to the printing delay. The bracketed information on proprietors is from a memorandum of the agent of Boulby Alum works - George Dodds (see below) dated 15th March 1780.¹²⁷

Thus three data points are included in the table and we can see that both plant survival and ownership were a risk laden business. One of the interesting demises is that of Cooksons plant, Cookson being a noted glass manufacturer in South Shields who was able to use his waste as alkali (see below page 62). Some of the information is not wholly consistent with other sources - No 8 - according to Young - was commenced by Sir Bryan Cooke and is "stil" carried on by Messrs. Cook; yet Dodd's 1780 memorandum shows Mallinsons as proprietor; No 20 in 1780 was owned by Yeoman but by 1817 the co-partner of Baker- Ralph Jackson - was involved here also; No 23 according to Young, could be considered a re-opening of No 1 and No 11 is probably not a separate works since its liquor was boiled at Sunderland.

However, change of ownership or partnership can be seen in terms of investment and the number of plants is not as good a guide to production as the "No. of pans drawn."¹²⁸ (for production of plants see pages 95 and 96)

temp. so as to be ...
of the ... and ... stock of
liquor ...
The ...

A more useful guide to continuance of plants is the succession of agents or managers.

Plant Manager in North Yorkshire.

The proprietor's agent often had to deal with more than the alum works. He would often be involved in the management of farms nearby but this side of his work does not, directly, concern us here. The agents of the two alum works for which we have records demonstrated clearly their managerial positions in regards to the alum works as we shall see below. The fact that their correspondence often consisted of reports on stocks, usage and occurrence indicate^s that their proprietors were interested in the operations involved in the process also and occasionally involved themselves more intimately. (see page 8.)

This position of manager is interesting in itself. We regard the rise of the "managerial classes" as a modern phenomenon and in the history of chemical industry we are prone to meet entrepreneurs, develop^u of processes and owner managers but the indications in these records seem to point to a management group who were no^t owners or entrepreneurs and who delegated part of their function to clerks, alum makers, liquorment¹²⁹ etc. but were in charge of production, shipping, buying, hiring and firing and developing the works. The managers dealt directly with each other on many issues and appeared to form a clear group as illustrated by the report of one Bartholomew Rudd on the Loftus Works where he remarks on the "unsocial" nature of the then agent James Farquahson and claims that "other agents" rarely speak with him. Dodds¹³⁰ frequently refers to conversations with other agents on technical and other matters.¹³¹

The evidence of their function can be seen below when the process and its economies are discussed but to give a frame of reference the succession of managers will be traced here - it being understood that the evidence is incomplete in this respect since only¹⁴ one case is there a clear appointment and in no case is there a resignation or dismissal. The nearest approach to a "dismissal" or perhaps redundancy is found in the letter of Tower to Westgarth instructing him to commence winding up operations at Boulby.

Ralph Ward is the first individual we find writing to Baker, then at ¹³² Oxford, concerning the state of the works in 1743 but Ward had other interests ¹³³ and does not feature as a correspondent thereafter. He was in fact a partner with Conyers and subsequently Baker and was active in promoting the cartel; subsequently he sold his quarter share to Jackson. ¹³⁴

Thomas Wardell is first encountered in correspondence with Baker in a letter of ¹³⁵ December 1754 and remained as manager until his death in 1772. ¹³⁶

George Dodds was appointed manager on 10th July 1772 (see the "contract of employment" on page ¹³⁷ 41) but his contact with the plant appears to stretch back to ¹³⁸ 1755 where he is mentioned by Wardell. His correspondence can be traced to the end of the eighteenth century and we find letters to him from the Loftus manager William Usher in 1809. ¹³⁹ In 1817, both George Dodds and George Dodds Jnr. appear as subscribers ¹⁴⁰ to Dr. Young's History of Whitby and in 1823, Bains ¹⁴¹ "Directory" gives George Dodds as agent to the alum works at Boulby.

This period of 68 year involvement (1755 - 1823) and 51 years as manager (1772 - 1823) with the last day mentioned i.e. 1823 not necessarily a terminal one - seems an unlikely term of service for one man and it seems reasonable to suppose that at some point around, say 1804, George Dodds Jnr. took over. The choice of 1804 relies upon the contents of letters about ~~in 1817~~ that time concerned with Dodds' ¹⁴² health and is speculative since unless a third generation is involved, he appears ¹⁴³ to be active in 1817.

George Westgarth appears as clerk to the alum works in 1823 but seems to have become agent by June 1830. ¹⁴⁴ He is listed as agent in White's "Directory" of 1840 ¹⁴⁵ and is the recipient of the letter from Mr. Thomas Forster dated 9/1/1869, ¹⁴⁶ instructing him to commence closing down the works. In view of 1871 being given as the year when the works closed (see above page ¹⁴⁷ 36) it seems that the "running down" process must have included calcining and processing any raw mine already bared, and even ^t when the time seems excessive. This letter is reproduced on page ¹⁴⁸ 42. Westgarth's reply is also interesting in that he reveals the measures he has taken to train his son to take over from him. His son, Thomas,

We George Baker and Ralph Jackson Esquires do authorize and appoint Mr. George Dods of Boulby Allum Works our Chief Agent at the said Works; and do empower him from Time to Time to draw Bills upon Ambrose Lynch Gilbert Esquire for the Money which shall become due from him to us for Allum to be delivered to him in pursuance of the Contract or Agreement made and now subsisting between us and him; and to make such Bills payable to Mr. Wakefield Simpson of Whithy or his Order, and deliver the same to him to be placed to our Credit; and also from Time to Time to receive from the said Wakefield Simpson or draw upon him for such Sums of Money as shall be necessary for paying our Workmen at Boulby Allum Works and carrying on the said Works or otherwise relating thereto. And the said Wakefield Simpson is to be our Banker or Keeper of the Cash for which such Bills shall be drawn and delivered to him, and is to be Accountable to us for the same, having an Allowance of the Money he shall pay to the said George Dods or his Order under this Authority. Dated the tenth Day of July 1772.

Witness.

Geo. Pearson.

George Baker,

Ra. Jackson

7 Ellison Place
Newcastle on Tyne
9 Jan^r. 1869.

Dear Sir

I have had a meeting with Mr Baker today, and we have settled to stop the Boulby Alum Works as soon as the present stock of burnt Mure is worked up. - I have & therefore to request that you will at once cease all boring, drifting or cutting underwood, and in fact do away with every possible source of expence, both in labour and materials, so as to make the most out of the Works whilst they last. - I hope you will be able to get quit of the Rough Epsoms. - My Son took the sample to Mr G^r Alum and also ascertained that he is a trustworthy person.

If you have not already sent Mr Baker a cheque for £1000, I beg you will do so at once.

Trusting you will use every exertion to wind up the concern satisfactorily

I am Dear Sir

Yours truly
Thos. E Forster

GEO Westgarth Esq -

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had been alum maker since 1867 following the death of Thomas Dodds - is this a relations ?

The Loftus records reveal the following sequence of managers.

J. Readhead appears as manager in the years 1766 - 1769¹⁴⁸

James Farquahson is manager in the years 1777 to 1785, although the last letter to Farquaharson¹⁴⁹ seems of different character to the others which terminate in 1783.¹⁵⁰ Nevertheless, it was reported that Farquaharson had annoyed his employer, Sir Thomas Dundas, who was seeking a replacement and although Dodds had opined ... "I suppose this will blow over and they will not Part..."¹⁵¹ there are no further letters.

Thomas Napper appears as agent in 1788 and his correspondence continues through 1794.¹⁵² It is of interest here that a Lieutenant Thomas Napper makes an appearance in a letter of 1782 from which it appears that he is beholden to Sir Thomas for his commission. The handwriting is similar and only one index entry is made under the name of Thomas Napper.¹⁵³

Apart from on letter from Losh, Wilson and Bell to John W. Walker in 1802,¹⁵⁴ concerning potassium chloride which therefore establishes him as manager at that time, there appears to be a distinct gap in the record.

William Usher appears a manager¹⁵⁵ from 1807 through 1816 although a letter from Alexander Tod of that March indicates that Usher is ill and unable to discharge his duties to the extent that the farm labourers are neglecting their own.

Alexander Todd appears as acting agent in 1816¹⁵⁷ and appears again in 1830¹⁵⁸ where he is carrying out investigation yet the manager listed in the directories of 1823,¹⁵⁹ 1834¹⁶⁰ and 1840¹⁶¹ is William Hunton.

In the case of the other plants, occasional mention of the eighteenth century managers can be found in the correspondence and in the nineteenth century the directories, such as those mentioned above are helpful. Ure also acknowledges one Mr. Scanlon, agent to Lord Mulgrave.¹⁶²

However, the essential work remaining, which is too vast to be undertaken here, is to find the background, relations to owners, in his account of, education etc. of this eighteenth century managerial group. The above note will, it is

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hoped, make it unnecessary to repeat the descriptions of these gentlemen in the account following other than to give their names.

Alum Making

(a) MINING

The removal of the sandstone overlying the alum slates was the first practical requirement. This material was generally called "Rubbish" as Winter records (page 29).

This "Rubbish" was however the main building stone of the area and was exported to Newcastle. It was also used in making the stone cisterns for the works.

Winter claims it was brownish red and sometimes very hard and "even the softer kind of sandstone by exposure to the atmosphere is found to grow much harder so that it is very useful in building."

For this reason, there would seem at first to be more than one way to interpret the following entries in the monthly reports of George Dodds.

(a) "12 June 1781 Lett set out to — Firth and Co a piec of Rubbish to work and pump at the west end of the Middle Gallery."

or

(b) "23rd June 1781, Lett & set out to John Dobson & Co a piece of Rubbish to work in the bottom Quarry over the main west dess" and "the 163"

(c) "30 April 1782, in the course of this month Cleaned the main west dess & covering dess by making the mine fit for bringing to the mine heap and got two bargains of rubbish finished off with those which were begun to wrot last December and Lett other two bargains of Rubish to work one in the middle and the other in the Low Gallery." 164

This indicates contracting labour to do this particular job and paying the "contractor" rather than keeping extra men ^{on} the books - a practice still used today - not that this would involve any overhead charge as it would at the present day. In any case, the men would have been on day wage or paid by the yard (see page 20) and only paid for the days required of them. On the other hand it could also indicate that the marked out place was let by Dodds as agent and that he received payment from those who wished to take building stone from this site. Such an arrangement would reduce the works wage bill, obtain an essential service and attract income all at the same time.

Unfortunately Winters' comment that the coastal sites facilitate removal of Rubbish etc. is borne out by discoveries of waste deposits on the cliff faces.

The denses mentioned, as Young¹⁶⁵ described the "working face" of the rock wall, each at different levels, on ledges, to allow transport of materials mined to the Mine heap or the place where it was calcined.

Unfortunately the mode of operation mentioned above is not found in the next few years of the report. It may be that once the rubbish was removed no such further operations would be required for a considerable while. However, the "pieces" described do not seem large and in the subsequent reports there are innumerable reports of landslides of "Rubbish" and "Mine." Landslides were the main hazard of the alum workings although They do not appear to have caused great loss of life. This is a speculation based on the fact that in the managers reports only two^{such} deaths were reported and, bearing in mind the brevity of the monthly reports, these deaths are recounted at some length as for example

"8 Sept 1784, Wm. Wales, a labourer at the New Works, was this day unfortunately killed by a piece of mine falling upon him from off the rock above where he was picking." 166

The second death was of Francis Pearson, the liquorman, on 17th January 1785 (see below page)

The danger of slides was not merely an industrial hazard of the alum quarry but a danger experienced by all those living on the cliffs near the shore as when at Kettleness during the night of December 17th 1829, the cliff gave way and the inhabitants are said to have spent the night on board the "Henry" an alum ship lying offshore.¹⁶⁷ The dwelling houses and alum works were overwhelmed but the works were restored in 1831.

Young also records of Runswick

"... that, about 150 years ago, [which would be in 1667,] the whole village except a single house, sunk down in one night, the ground on which it then stood, which was to the south of the present village, having suddenly given away." 168

To which he adds

"It is stated as a most providential circumstance that most of the inhabitants were than night waking a corpse and that perceiving the approaching catastrophe, they not only escaped themselves, but alarmed the rest so that scarcely any lives were lost in the dreadful overthrow." 168

The alum shale was broken away from the face with picks and carried by barrow to the calcining sites by barrowmen as mentioned above by Wilson. The paths were provided with planks to make the way easier a fact illustrated by Wardell ^h _w remarking on the imminent demise of a nearby cartel breaking plant crows over their not having sufficient "barrow plank" to last the fortnight. 169

ROASTING THE SHALE.

The main observation of the other authors is the immense size of the calcining heaps. This was criticised by those who drew attention to the Hurlet heaps which were lower. After Colwall's clear description of the heap broken up into self contained unit^s, the latter writers seem to fudge the issue that the heap was in fact many heaps. Dodds reports that

"27 June 1781 ... finished 1st division of our Mine heap" 170

and subsequently

"26 April 1782 ... begun with the 2nd division of the Mine heap by setting a fire in order to burn mine." 171

This fits more with Colwall's picture and indicates that the advice of Ure to provide continuous supply of mine was in fact a feature of the management^e of plant long before.

The following longer passage amplifies the point - the underlining is my own emphasis.

"(2 October 1779,) I now begin very much to doubt we shall not be able to keep all our fires in through the winter, we have not a force of barrowmen at all competent to the consumption of burnt mine - the pitmen have already brought down two considerable shots of hot mine - another shot which we daily expected down is all they can have - till that part of the mine heap which is still burning is finished and partly cooled." 172

The situation in the winter of 1794 must have been as bad or worse when Thomas Napper informs Lord Dundas that there was not a barrow full of burnt mine at the Boulby new works and not much in the old works. 173

The cause of the problem according to Dodds, the manager, was a manpower shortage as is already implicit in the last quotation. He gives this justification in the same letter quoted above.

"I do not assure you I have exerted my utmost abilities to prevent a reduction which I know will be much to our loss but what can be done - when so much depends on manual labour which is not to be got." 174

The problem of labour shortage in Dodds' view was not, however, simply insufficient total material in transit but that also the 'tempo' or "regularity of loading" the heap was affected.

"(19 Feb 1780,) A great loss arises for want of men to carry on the heap briskly for when there is not a quick succession of mine, the fire dwells too much in it and entirely destroys or evaporates the fine crystals of alum - which it is intended to generate again - the operation being retarded." 175

This explanation arose from his prior observation that he

"sorry to observe that we are not likely to do so well in making alum as last Spring - our mine seems so much burnt." 176

Which seems to support the view of most of the commentators that the main 'test' of effective calcination was a visual agessment.

Dodds reports a manpower increase in April 1780 and claims it has improved calcining a great deal, the heap being "the best and briskest I have seen since the year 1765" and in May of the same year (1780) claims that the alum making is going well and that also

"next to this ... the burning of the mine on which the other so principally depends is likewise doing well. Hands come in most of which I set on for by the mines we shall soon get a good and capital mine heap." 178

The need for great care in organising and planning the divisions of the heap and supervising the sequence of firings and the piling of the heap is due to the fact that once commenced, a considerable time must elapse before the heap is ready for use - as evidence in this entry.

"5 August 1786, finished the taking away all the mine from the small heap made in the East End of the new works which was begun 14th Dec 1785 and finished 24th March last and which contained about 150 pitts." 179

This indicates three months burning followed by an unspecified cooling time. However, this may be accounted for by the size of the heap. In a further entry, a fire was set on June 2nd 1784, kindled June 10th 1784 and finished 7 August 1785 indicating a total "calcining and exposure" time of 14 months.

It appears that on this part of the works processes the commentators generalise and simplified too much and the works practice was to treat the heaps individually rather than adopt some standard calcining time.

However, evidence for the unusual height of the heaps is found in the use of

gantrees and bridge to handle material.

"11 July 1782, set up the gantrees on bridge from the middle high floor to the mine heap." 181

The quantity of mine produced by calcining was assessed at this^e no of "pitts" it would fill and the task of transporting the mine to the *leaching* pits was presumably the task of the pitmen mentioned above who carried the burnt mine in barrows to the pits which were situated close to the calcining site.

Leaching the Mine A) The pits.

Some guidance as to the size of the leaching pits is found on a loose page at the back of the "Experiment Book 1829" of the Loftus works.

The "old pits" were 72 ft long 18ft broad and the depth empty was 3ft 2 in deep at the deep end and 2ft 8 in deep at the shallow end. Filled with mine the depths were respectively 2ft 6 in and 1ft 10 in. This was assessed as giving a content of 108 yards of mine (assuming that these depths for mine are depths of mine in the pit and not the dipstick depths when filled with mine i.e. depth to top of mine layer, and assuming a trapezoid profile, the cubic capacity of mine works out at 104 cubic yards.)

The note records that it requires 44 scores of barrows to fill this pit.

Winter describes the pits as usually containing 60 cubic yards of liquor (assuming increases in depth when water added?) and Colwall's dimensions give pits of about 80 cubic yards (90 cubic yards also on above assessment) which required 40 score barrows to fill them. The small new pits had a capacity of 36 yards (38 cub yards as above) require 16 score barrows.)

The great variation in the possible size of the pits does not allow an easy check on the overall size of the heaps mentioned by the commentators. In the case of the small heaps of 150 pit mentioned by Dodds, the various dimensions above give a volume of burnt mine varying from 5700 cubic yards for the small pit through 9000 cubic yards for "Winter's pit" to 15,600 cubic yards for the old pits at Loftus. It is possible that the bulk of the original heap was twice that of the final heap ~~was twice that of the final heap~~ although the practice of loading the heap after the commencement of calcining makes the "original size of heap" seem an irrelevant and positively dubious quantity since the material

was being consumed at the same time as more material was added.

In view of this, Ure's figures of 10⁵ solid yards in the heap appear to be irrelevant to any discussion of alum making.

B) Leaching

There is no description in the regular reports of the sequence of rotation of the mine or liquor in the pits - it must again be assumed that the practice was too well known to the corresponding partner to warrant description. However, on the occasion of the new works opening at Swallow Tree Hole in 1784, Dodds made a rare reference to the production of the raw liquors in the monthly report which show the gradual concentration by rotation of liquor and mine and its testing.

"20 Oct 1784, fil'd one of the new pits at New works with burnt mine and water to make liquor.

"21 Oct 1784, fil'd 2nd pitt at Do.

"27 Oct 1784, weighed the liquor taken from the pitt last filled at New works and found it 8d weight." 184

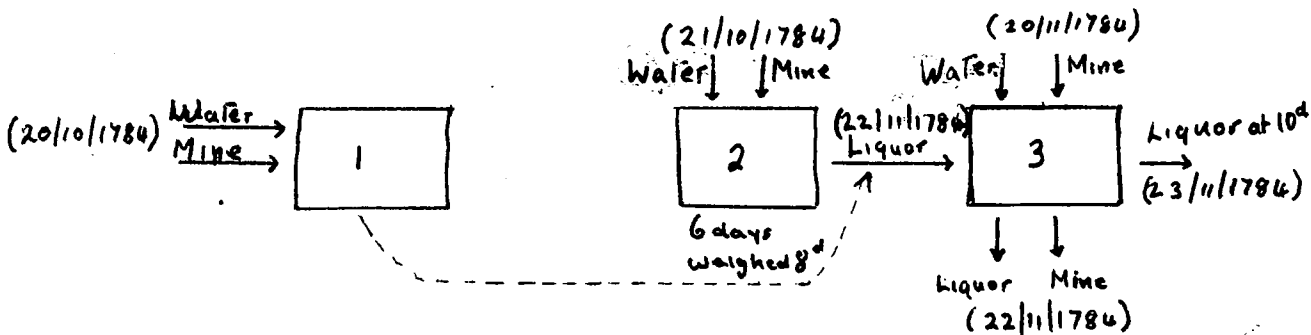
"20 Nov 1784, fil's 3rd new pitt with burnt mine and water at New works.

"22 Nov 1784, empties Do and filled again with burnt mine and liquor ...

"23 Nov 1784, run the first liquor from New works to alum house from the pit wrought yesterday weight 10d" 185

Taken by itself, this report gives no definite duration of steeping which seems to vary from one to five days, or whether there is an overall flow of water countercurrent to the mine. The term "burnt mine" does not indicate whether it is fresh from the heap or previously steeped. Indeed, the purpose in giving this information in the monthly statement must be to demonstrate Dodd's Success in "commissioning" the New Works for whose creation he was responsible.

If we, however, consider this report assuming the "countercurrent flow" practice mentioned by the commentators a possible flow route could be as follows:



This is by its nature tendentious since the source of the liquor on 22/11/84 could be pit (1) or pit (2). Pit (2) seems more likely in view of the time lapse. However the steeping time seems to vary considerably

This may be due to the setting up of the new works or it may be that steeping at each point of the rotation was taken up to a "preferred weight" or that "weighing" was carried out each day and the liquor transferred, following a satisfactory density being achieved. These are not identical since in the first case more "analyses" would be required whereas in the second case a daily test could lead to a variation between the "weights" of different batches which seems indicated below. The above memorandum indicates that a "weight of 10d" - pennyweight - is suitable for raw liquor. A few months later in a letter of 4 February 1785, Dodds, still reporting the progress of the new works, gives his guideline for the raw liquor more fully.

"Our liquor from new works has been increasing in its weight, the other day as high as 15d we have only one instance of the old works exceeding the weight. I rent for once at 16d, at this weight it is too heavy for making alum must be reduced by weaker liquor to about 11d or 12d which gives the greatest possible production of alum".¹⁸⁷

This range of weight is similar to that quoted by many of the observers eg Winter "11½-12 pennyweights" which give corroboration to the fact that the observers were to describe a control technique in use in the industry instead of giving a prescription for their more learned readers (although to be fair it is only very few who give this latter impression).

The technique of measuring these "weights" or gravities - the "alum makers secret" - is in any case described by Young above (see page 34). It is a simple technique to use; a sample could be collected by any operative and either the balance - which could possibly be a simple two pan hanging variety - used in the works or the bottle carried to a room used for the purpose. In support of the latter view, one can cite the view of the Cleveland Industrial Archeologist who discovered at the Boulby site a room which, they believed could be a laboratory.¹⁸⁸

More significant still is the booklet in the Loftus records entitled "Experiments in Laboratory 1805"¹⁸⁹ which is transcribed in full as Appendix 1.

This booklet contains a number of experiments but of direct relevance, here, is the data on pages 26 and 27 which have been copied as pages 51 and 52 of this account. This is a comparison table of alum makers' weights in the first column - based on the standard 80 parts - against specific gravity in the third column and hydrometer readings in the fourth column. Column two seems to refer to an "alum makers weight" based on 100 parts - perhaps this was used for a particularly large "assay bottle".

Jan'y 18th 1806

1/2 lb Brimstone Ashes from London taken with 1/2 lb of Potash with all the Salt was extracted. The residue I put into an iron Pot & poured down to a Dry salt to see the weight of the residue. Bk. 10. 5

Weight of the Potash is } 7. 1. 10
Dry salt

Weight of the residue is } 0. 7. 2
One Ton of Brimstone Ashes will yield 2. 3. 26 Dry Sulphate of Potash. —
The 3 pounds of the Brimstone Ashes used in the Experiments were dried. These the sample from London. —
1/2 lb Brimstone Ashes extracted with one lb Potash salt water.
Ley — B.

1/2 lb Brimstone Ashes extracted with one lb Potash salt water.
Ley — B.

January 21st 1806

M. 2 Glass set as 22nd of 11th source of New way sulphate of Potash from the Brimstone Ashes — Prussia 3. 12. 0

S. 3 — Glass set same as the above with 1 ounce Muriac from Balmien — Prussia, 5. 2. 0

RECORDED
SERIALIZED
INDEXED

Apay 1000 lbs. Hydrometers
 800 lbs. 29

Sp. Gravity	Hydrometer
9 1/4 - 11 1/3	23
9 1/2 - 1.106	
9 3/4 - 1.115	
10 - 1.118	
10 1/4 - 1.120	25
10 1/2 - 1.125	26
10 3/4 - 1.128	
11 - 1.130	26 1/2
11 1/4 - 1.13 1/4	
11 1/2 - 1.13 1/2	28

Divide the Specific Gravity
 by 16 gives the number of
 grains in the cubic foot

There is 15 grains in each Dip
 of the Apay bottle. Multiply
 each Dip by 15 to which add
 1200 grains being the weight
 of the water inside the men-
 total by the number of grain
 that gives the specific gravity
 and by others to the standard.
 which you get to figures in
 the standard book of the left
 hand page for the grades
 Comply them of any bottle 1590 grain
 29 1/2 1.115
 29 1/4 1.115

Example

15 grains in each Dip
 Multiply 10 the weight by the 150
 Add 1200 grains the weight of the water
 Multiply 1300 hydrometers

1200) 1350.000 (1.125 Specific Gravity
 which is about 26
 by the Hydrometer
 150
 1200
 3000
 2400
 6000
 6000
 1230
 and add the index

Certainly the use of a measure with 100 parts is not recorded elsewhere unless the half pint bottle of Colwall containing a 120 pennyweights of water be included. The remainder of the two pages shows calculations needed to convert from hydrometer readings to pounds per ^{cubic} feet and from alum "weight" - at 80 parts - to specific gravity.

The use of the "assay bottles" is also of interest since Turinton, describing the use of the density bottle in the same way as Young asserted that "there are no notices of any such bottles in the accounts but assay dishes also called proof dishes and purchased from time to time at 4d each ^{or} $\frac{3}{6}$ a dozen probably served the same purpose" and this indicates that the practice was general in the area. Watson claimed in 1854 that his brother possessed a bottle which was 200 years old.

The hydrometer readings are approximately $2\frac{1}{2}$ times the "alum makers weight" which indicates that the instrument was almost identical to the Twaddle hydrometer - ^d ^A Ure's statement that "the numer ^b ^A on Twaddle's hydrometer divided by 2.5 give alum makers pennyweight." ¹⁹⁰ The relation between Twaddle and Mackintosh of the Scottish alum works will be taken up below ¹⁹³ but it is surprising that Ure's conversion factor above is found in his "Improvement" of 1845. In the first edition of his dictionary of 1839 he gives only densities.

The densities obtained using the "assay bottles" - which were not totally identical, as shown on p.5 of the "Experiment" book - seem to demonstrate glaringly the error of spurious accuracy. The raw liquor tolerance of 10d - 12d is a density range of 1.13 to 1.15 and the very high result of 16d quoted is 1.20 and this is obtained from a $\frac{1}{3}$ pint sample in a large pit - perhaps unstirred ("steeping") - containing a Burnt Mine sample of variable composition, covered with water, which would take some time to realise a homogeneous solution through the action of natural diffusion.

On closer examination however, we see that the steeping time is at least 24 hours and may be much longer as mentioned above. A sample taken at the end of this period - by tying the bottle with string and immersing (say) half way down - would have a fair chance of being representative and mixing is facilitated

over the period of leaching by the rotation of the liquor and mine around the pit system. If we accept that the samples are representative, then an interesting picture emerges.

The pits have a capacity of 60 cubic yards - according to Winter - and a difference of one pennyweight in the "weight" corresponds to a change in specific gravity of 0.0125 or a weight change of 1.25% in the mass of solid dissolved in the liquor. In the 60 cu. yds. pit, this corresponds to a change in mass of $62.3 \times 9 \times 1.25 \times 10^{-2}$ pounds ($1 \text{ft}^3 \equiv 62.3 \text{ lbs}$; $1 \text{yd}^3 \equiv 9 \text{ft}^3$) i.e. 420.5 lbs or 3.75 cwts. The same tank containing a liquor at 15d would, by the same calculation contain 15 cwts ($3/4$ tons) more dissolved solid than a liquor of 12d and the difference between 10d and 16d represented a total weight difference of 22.5 cwts.

The Loftus large old tanks, mentioned in 1830, when they were in use would exhibit the above total weight difference multiplied by a factor of about 1.7.

It is apparent that such weight variations could have a major effect on the subsequent steps especially the time required for concentration and amount of alkali required.

It was suggested by some observers that "used" but not "exhausted" mine could be and was in fact, recycled to the mine heap. Dodd's monthly reports contain no references to the practice and Todd's investigation in 1830 indicate that it was not a common practice. The investigation was either initiated as a result of the Boulby works prior results or else both Westgarth and Todd were working on the same lines. The correspondence concerning these investigations are worthy of note.

In a letter of 3rd September 1830, Todd stated that the experiment to determine what quantity of used mine a portion of new mine would impregnate was going well and achieving results similar to that shown him by Mr. Westgarth where he got 1 part good alum from 8 parts shale as opposed to the usual result of 1 part good alum from 80 parts of shale.

A further corroboration, if it were needed, that a "works laboratory" existed at the plant, Todd, in the same letter, describes how he took his sample

to the alum house and steeped it. He recorded the solution as

"very strong in the sulphate of ammonia and what was very important gave with the usual tests no traces of lime or magnesia and comparatively very little iron showing that these had been dissolved out in the first lixiviation." ¹⁹⁷

This indicates the use of at least spot tests of a qualitative nature to identify species and since we also have earlier evidence in the 1805 ¹⁹⁶ booklet of quantitative assessment on alum production using different alkali sources (see page 51.) it seems reasonable to propose that scientific control and testing materials was carried on at the Loftus plant at least between the years 1805 to 1830 and bearing in mind that chemical appreciation of the process was growing throughout the period (see account of Ure, Knapp etc.) it seems more reasonable to suppose that it continued beyond 1830.

The extent of development trials is brought out by Watson in 1854 who described many unsuccessful ones of the 18th and 19th centuries. ¹⁹⁹ This is, of course, in addition to the continuing use of operational controls using density which are reported by all secondary accounts throughout the remaining life of the Yorkshire process (i.e. up to around 1870)

SETTLING

The archaeological survey makes no mention of setting tanks in their written account but in one of the diagrams a group of pits or tanks are labelled "settling tanks". ²⁰⁰

The liquor passed into cisterns and we find mention of a unit called a liquor cistern in the estimates for the new works - opened 1784. ²⁰¹ The settler in the estimates refers to a later step in the process. Also during building of the new works we find a memorandum of June 1784 noting that a cost of £9.13.0 had been incurred in construction "Pitts, cisterns and other buildings." ²⁰² This must have referred to the work of putting in the wood supports and/or lining the walls with clay since the much greater cost of £249.10.9½ is mentioned in the previous entry to "Space set out for Pitts and Calcining Place." ²⁰³ Although no mention of settling as a unit operation is mentioned, in the Boulby accounts, there are numerous references in the monthly remarks to the cleaning of tanks and cisterns.

These operations are mentioned in the report of the excavations where

"traces of calcined shale" are found on the cliff face. ²⁰⁴

There were "three cylindrical cisterns sunk into the ground and built of curved sandstone blocks". The middle cistern had a diameter of about 4 metres and depth of about 2 m. giving a capacity of 25 cubic metres. The author of this account - S.K. Chapman ²⁰⁵ - draws a picture of the problem of digging out the cistern and emptying it against the prevailing wind. It seems that this operation was either not considered as such or regarded as too obvious to mention. The chemical importance of the settling process is brought out later by Ure, Knapp et al. ²⁰⁶

CONCENTRATION OF THE LIQUOR.

The liquor was brought to the alum house for concentration. At Boulby, this was achieved by a culvert leading from the new works (at a higher level) to the Alum house, ²⁰⁷ Again, the particular unit operation of concentration is not emphasized in the manuscript accounts.

The liquors are heated in pans - metal vessels usually made in situ by site craftsmen - and the names given to these pans show a considerable diversity with presumably a diversity of uses. We find, clarifying pans, drivers, slam pans and roaching pans. ²⁰⁸ By a simplistic process of elimination, we can eliminate roaching pans and slam pans as not used in concentration. It appears from the Loftus accounts that alkali is added to liquor in the clarifying pans ²⁰⁹ - but is this after concentration in the same pans? The drivers have a suggestive name in respect of concentration by evaporation but without further evidence no firm distinction may be made. The evidence for concentration as a separate step comes once more, from the reports of the "learned authors of Dictionaries of Arts."

PRECIPITATION OF THE ALUM POWDER A) The Alkali.

It was during this operation that 'alkali' was added to the liquor to precipitate alum powder. The use of the term alkali is prevalent in the accounts and perhaps demands some explanation. That the "alum liquor" was acid is beyond doubt and its acid properties were used in the seventeenth century tests for the quality of Urine supplies (see page 23).

However, the alkali used was weak and was supplanted eventually by a non alkaline substance muriate of potash. Therefore although the term alkali will be found in the following account, the mental reservation that its purpose was to provide potassium ions to the liquor could usefully be made.

This operation showed the greatest change of the years covered by the manuscript evidence in that the source of raw materials and their nature and hence their preparation and control in use changed.

The alkalis used initially were kelp and urine. The extensive use of the latter is brought out in the accounts of Young and Colwall. Their allusions to human suppliers seem borne out by Watson's ²⁴⁰ descriptions of the methods by which urine was collected from houses and farms by pack hors and paid for by volume using a standard vessel containing ²⁵ galls. However, it seems likely the predominant supply was from animal sources and that arrangements were made in cattle byers to channel and collect this commodity. The extensive records of "Urine Carriage" with prices and supplies occur continually in the Boulby cash account and the stocks and monthly use of this substance were recorded in the Managers' monthly report. Although the urine was 'alkaline' in the sense that its ammonium carbonate content was neutralized by the acid in the liquor liberating carbon dioxide - which ¹ was the basis of Colwall's test - it seems unwise to strain the loose definition given above any further since urine supplied ammonium ion to the liquor and, throughout the time of the joint usage of urine and a potassium based alkali, mixed ammonium potassium alum was the product of the plant. A typical 'Urine Carriage' entry is reproduced on page ⁵⁸ showing that in March 179⁴ ²¹¹ deliveries were almost daily and the deliveries of urine were still being noted in the early years of the new century.

Kelp, ²¹² the main alkali in the seventeenth and eighteenth century has been the subject of many investigations by economic and technological historians.

In simple terms, it is made by calcining selected types of seaweed. The "ash" produced is kelp or kelp ashes and by leaching the ashes, a solution called kelp lees could be obtained.

The manufacture of kelp in Scotland is well known and the boom which took

use.

Tradersmen's days about the Old House

days	1794 May	days
25 ✓	Henri Adanson Carpentier	27 ✓
19 ✓	Geo. Hoggarth - d.	27 ✓
25 ✓	W. Hebyer Blacksmith	27 ✓
21 1/2 ✓	Jam. Jackson - d.	27 1/2 ✓
23 ✓	Nich. Gate - Mason	13 ✓
22 ✓	Robt. Calvert - d.	24 ✓
21 ✓	Robt. Calvert jun. d.	24 ✓
"	Phil. Herivelton Thatcher	3 ✓
24 ✓	Robt. Nelson Sabourin	16 ✓
"	Gill. Cooley - d.	26 1/2 ✓

Urine Carriage May 1794

1794 May	Jos. Thomp-son		Dnity Thomp-son		John Pether-son		Margt. Webber-Sothers	
	Tons	Loads	T	L	T	L	T	L
1	1		6					
2	6		6		6			
3	"		6		6			
4	Spnd							
5	"		6		6			
6	"		6		6			
7	"		6		6			
8	"		6		6			
9	"		6		6			
10	10		6		6			
11	Spnd							
12	"		6		6			
13	"		6		6			
14	"		6		6			
15	"		6		6			
16	"		6		6			
17	6		6		6			
18	Spnd							
19	3	1	6		6			
20	3	1	6		6			
21	"		6		6			
22	"		6		6			
23	9		6		6			
24	10		6		6			
25	Spnd							
26	"		6		6			
27	"		6		6			
28	"		6		6			
29	5	1	6		6			
30	"		6		6			
31	3		10		6			
	23.8	15.0	8.4		2			

Tons Loads
47.2 ✓

place during the potash and barilla famine in the late eighteenth century can be found in the ~~xxx~~ records. ²¹³

The Dundas family who owned the Loftus works could rely on their Scottish interests as is brought out by the correspondence between Sir Lawrence Dundas and Thomas Lindsay ^{213a} where the latter estimates that 82 tons could be produced from the six sites on Sir Lawrence's shores in Orkney in the year 1781,

At about the same era we find George Dodds at Boulby corresponding with Messrs. Knox and Co. of Dunbar. ~~Writing in~~ Writing in 1778, he offers £4.10 per ton with the proviso that he will go as high as £4.15 on the "usual terms". ²¹⁴ This cargo appeared to be of 57 tons.

Such coastwise traffic was prone to disruption at this time due to the activities of ~~enemy ships~~ ²¹⁵ who in 1779 had been sighted along the length of the north East coast.

Boulby was hit by the privateers in 1781 as shown in the following extracts from the monthly reports for July and August of that year.

("By 31 July) a French privateer run the Violet on shore. Coal laden a little below water mark about 200 yards to the West of the outpost the privateer people set out boats to get her off - which they could not effect then they set about destroying her but were prevented by people firing upon them from the top of Newfell." ²¹⁶

In view of developments in the use of alkali it is interesting to note the claim that Lord Normanby's works used kelp as late ²¹⁷ as 1845.

The Scottish kelp was by no means the sole supply On September 19th 1778, Dodds wrote to Mrs. Baker to inform her that both the 'Scotch' and Creswell kelp had arrived. ²¹⁸ In the next year he writes that

"Mr. Daniel has now recd the Hartlepool kelp and it is agreed that it and the Creswell kelp be all at a price without any deductions." ²¹⁹

These local supplies seem to have been more than simply purchasing a commodity. Dodds seems to indicate a greater contractual involvement when in a note of Feb 2nd 1773, he

"Agreed with Nicholas Hartley to burn kelp on Creswell Scars the ensuing season at £1.12 per ton." ²²⁰

Similar agreements were made with James Cuthbert of Whitburn - Feb 10th; Leonard Volum of Hartlepool - Feb 16th ²²¹ and Richard Gates at "Sunderland and Riop Scars" - March 1st; ²²³ and on August 7th 1779, he remits £40 for one years ²²¹

224

rent on Creswell kelp rocks.

This local supply was and continued to be a major source and Dodds notes that between 19th and 29th July 1782, he had

"bought considerable quantities of kelp on the Durham and Northumberland coast." 225

A much clearer picture of the extent of the available supply of kelp is given in this extract from one of the notebooks in the Boulby records. 226

"Robin Hoods Bay	20 tons	under £3 per ton
Staithes	20 tons	£4:10
Hartlepool	30 tons	£2:10
Blackhall	6 tons	£4:10
Horden	10 tons	£4:10
Seaham	14 to 20 tons	£4:10
Sunderland	}	
Ryhope		
Whitburn		
Creswell	40 tons	£3:10
Coket Island	15 tons	£4:4
Bomar	80 tons	£4:4
Do	70 tons	£2:17:6
Beadnel	18 tons	£4:4:0
Total	<u>381 tons</u>	

The attitude to supplementary sources of alkali seems ambiguous. On the one hand was the scarcity of kelp and its high demand. On the other hand, a natural caution towards an untried raw material. We see this clearly in the reaction to Fordyce's "British Barilla" which came on to the market in 1780. Dodds had written of Fordyce's plans on 26th February of that year. 227

Dodd's comments was that "even the name of it would be useful in bargaining with the kelp people" and reports later 228

"(Mr Mallinson's agent) apprehends kelp will be more moderate than expected as the British Barilla and Hull ashes will undoubtedly answer the purpose of alum making." 229

Kelp Bergins 1782. by G Dodds 1, Journey July that yr

Robin Hoods Bay	20	under	3 ⁴ p. Ton
Heaths	20		4-10
Wallepool	30	on an sy	2:10 it fell short
Black Hall	6		4-10 - by Gates 11
Horden	10		4-10 by Ra lolling
Prachem	14 " 20		4-10 by John Kettle - seen at 8 ^a
Lunderland	} 58	u	4-10. Heavy
Kyehope			
Whithorn			
Oriskell	40	11:20 to	3-0 - made by John Kettle
Lochal Island	15		4-4 Short
Bomas	80		4-4 Barber
Do	70		4-4 by
Beednal	18		4-4:0 Pringles

Total - 381 Ton
 minus 4
385

Mem. Woods help at
 Beednal, good for kething
 7 quarts brought by one
 Derry day 55^d
 Dnyhorn

G Dodds L. 1100 19 Oct 82
 got in the kelp makes out 404 Ton - Less of Pak
 looks out in a 3^d of kelp

Nevertheless, there was a variety of alkali in use in 1780 as is shown in the memorandum "Enquiries relating to several alum works" of 22nd Feb 1780²³⁰ (the middle column gives an idea of the 'size' or production capacity of the plants and we can say that a pan produces per month 6 tons" according to a memo of 15th March 1780.²³¹

Further to this in a letter of May 13th 1780 to Knox and Co. of Dunbar, who supplied kelp, Dodds shows a more complete awareness of alkali supplies currently available although since the letter is concerned with price negotiation, it may be that not all the supplies were equally suitable; he wrote

"We expect the price of kelp will be much lower than was expected early in the year - many circumstances contribute to this - as the taking off of the duty on potash and giving a bounty on their importation, the Manufacture of Barilla at Shields and the method the Glass works pursue of boiling down salt water which with a cheap alkali answers the purpose of kelp ~~besides~~ besides the use of sandibar and soap ashes now going forward with success at three out of eight alum works."²³²

He identifies the three works in the memo of February 1780 mentioned above where he tabulates the information thus.²³³

<u>Works</u>	<u>No. of pans drawn</u>	<u>Their Alkaline Material</u>
Peak	5	Kelp & Sandibar (sic)
Stow Brow	2	"
Saltwick	3	Kelp, Sandibar & British Barilla
Eskdaleside	3	Kelp
Sandsend	5	"
Kettleness	2	"
Boulby	4	"
Lofthouse	fires out	"

Saltwick was owned at this time by Cookson and Co. who had interests in glass manufacturing at South Shields.²³⁴ It was natural that they should then attempt to use "sandiver" and in fact they had approached Mrs. Baker of the Boulby plant to interest her in this product. On her writing to Dodds, he replied

"... I note your conversation with Mr. Cookson. I have been told of the matter they skim off the glasshouse furnaces- they call it sandibar - it would not answer at Mr. Cooksons Works but I believe they use it at Mr. Mallinson's along with kelp and they say it answers the end but I should not like it."²³⁵

He obtained a sample of British Barilla in September of the year.

By the late 1780's, Boulby was using a mixture of kelp and soapers ashes and, of course, urine. Initially, the accounts of kelp, ashes and urine were kept rigidly separate in the monthly report but eventually kelp and ashes were reported together. (see the managers accounts reproduced on pages 64 and 65)

~~The effect of using soapers ashes is brought out in a letter of Dodds dated 24th December 1785 (which appears to be about the time when they first were introduced.)~~

The effect of using soapers ashes is brought out in a letter of Dodds dated 24th December 1785 (which appears to be about the time when they were first introduced.)

"I have pleasure to tell you that the Fox was safely delivered of the abhes the other day and we are now getting them up the Gin - they look exceedingly well... the house we have bought them off can make about 240 tons per annum which is better than 480 tons of kelp so that when these ashes come to be generally made and used, kelp must be considerably reduced." 237

On 31st December 1785, Dodds explains that they are using a little of the ashes and that the "Lees are much mended" by which he appears to mean that the ashes are enhancing the gravity of the alkaline solution (see below.)

The consumption of alkaline materials for 1787 averages at a monthly figure of 25 tons kelp; 7.5 tons ashes and 46 tons urine costing per ton £4:16 (approx) £5:12:6 and 8s6d respectively and in October of 1787, Dodds records 239

"Finished our kelp season

	tons	cwts
Kelp laid in	236	12
Black ashes	110	5 "

We also know that both these staples continued in use after the turn of the century. In 1809, William Usher, agent at the Loftus works writes to Dodds as follows 240

"... Lord Dundas has desired me not to dispose of any of the kelp until the month of March next. However, to serve you as a good neighbour and having always found you ready to accommodate Lord Dunas' works with ashes or anything else, I am happy I have it in my power to serve your present wants."

By this time, the substances used by the alum maker either instead of, or in combination with, kelp and ashes were clearly non alkaline products and these were the muriate and sulphate of potash.

A reference to the use of muriate of potash occurs in 1802 - and this is the earliest reference I have so far found in the manuscripts - where in a letter Losh offers Walker (the Loftus Agent) granulated muriate of potash. ²⁴²

This corresponds to Dr. Young's date of 1801 for the introduction of this identifiable chemical species and since the Loftus works were

"separated from the Boulby works by a narrow ridge of rock left as a boundary by the workmen of the respective proprietors." ²⁴³

it would seem reasonable to suppose that they would operate almost identical processes and therefore adopt muriate of potash at much the same period. This supposition would be strengthened if the agents were seen in regular communication and the letter so far quoted seems to indicate this to be the case. Furthermore, the author of the above passage the Rev. John Graves, writing in 1808, having described operations at Boulby saw no point in describing separately the similar operations at Loftus and Winter ²⁴⁴ groups them together as the most scientifically organised plants (see page 76)

Graves however, stated the alkaline materials to be kelp and urine, whereas we know from correspondence already quoted that muriate of potash was in use at Loftus at this time. In the case of Boulby, there are no managers reports for the period and the very brief account (annual) of 1804 ²⁴⁵ refers only to "alkaline salts."

Perhaps this striking inconsistency in the records can be understood if we look at the origin of the muriate of potash which was supplied to Loftus by William Losh and his associate ^S.

William Losh, on his biographer's testimony, ²⁴⁶ seems to have been educated to the practice of chemistry and chemical industry in a way reminiscent of that education accorded James Watt's son. ²⁴⁷

Losh, in early youth completed his education in Hamburg where he made friends with his "fellow student Alexander von Humboldt." After spending some time in

Sweden learning the language and metallurgy, he went to Paris and was there studying under Lavoisier at the time of the revolution. From whence, he returned to join his brother and Lord Dundas in developing alkali manufacture.

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The report of the British Association meeting of 1863 in Newcastle on Tyne contains an historical account of the synthetic alkali industry on Tyneside and indicate^s W. Losh and others as commencing a works in 1796. Various processes were attempted among which was one

"founded on the mutual decomposition of common salt and sulphate of potash. This operation was regularly carried on by Mr. Losh and Mr. Doubleday whenever the ~~prices~~^s of the the two potash salts (~~read price of the two potash salts~~) allowed a profit being made and chloride of potassium was as regularly sold to the Yorkshire alum makers." 249

This indicates that the supply was intermittent, which also seems to be inferred by a letter of 16th January 1808 from Usher to Losh, where, noting receipt of an invoice for previously supplied muriate, he desires to be advised of any more such on the market.²⁵⁰ When none was available, there remained the other alkaline materials and it appears that far from endorsing Young's orderly and sequential progression of alkalin^e materials - one supplanting the other - the available evidence suggests a "mixed" alkaline lees. From early times, both kelp and urine were used together to proddce a mixed alum, although it must be added that in the Managers monthly accounts, the usage of kelp and urine were accounted separately and stored separately. However, in these reports, the initial subdivision of the kelp stock account into "kelp" and "soap^res ashes" eventually became a "kelp and ashes" account^{as} and mentioned above, in the brief annual account of 1804, the only commodity accounted is "alkaline salts." This is interesting since a payment for urine can be found as late as 1807. Winter, in his above account, also appears to describe the use of a "mixed" lees, the important criterion in the addition of which seemed to be the attainment of a desired decrease in density in the alum liquor - and therefore in total dissolved solid. The use of the work "or" in his description would be in support of the idea which seems to be borne out by the details of alkali preparation below that the different substances were leached and dissolved separately and added as

available to achieve the required gravity. Dodds fudges this idea - perhaps he negates it - when in his letter of 31st December 1785, he comments that "we are using a little of the soap^s ashes ... find our lees are much mended." ²⁵² Subsequently to this, Dodds buys ashes and kelp during each season.

Although the use of muriate and sulphate of potash eventually supplanted the lixiviums of ashes of kelp, soap^s ashes and sandiver, it is open to question whether these early supplies of a 'pure' chemical competed well with the extremely variable and substantially insoluble "ashes."

From the letter of William Usher to Losh we learn that

"(24 Dec 1802) the sulphate of potash is generally such a dirty article and bad to dissolve that our alum maker does not wish to use it when he can get good muriate." ²⁵³

A letter of 3 May 1810 ²⁵³ informs Losh that the alum maker has tried the muriate and that sand and a "black matter" are precipitated when he made a "ley" ~~since~~ from it. Usher goes on to say that his alum maker would prefer a "clean salt" since he can use it dry, whereas he would need to lixiviate this impure material to purify it. Later in 1812, ²⁵⁴ Usher is complaining again that the muriate is adulterated with black insoluble matter and also that it contain a large proportion of magnesium chloride which interferes with the process.

However, in the long run, a substance that was predominantly a single chemical specie became the sole "alkaline" additive, although, at this point, it must have been clear that the object was to add a salt of potash to form a potassium alum.

By 1854, kelp had been "long since laid aside" and "muriate and sulphate of potash and sulphate of ammonia are now generally used" - the potash salts being obtained from kelp. ²⁵⁵ William Watson who supplies this information in his "Guide to Guisborough alum works" states that 1 ton of the commercial salt would produce $4 - 4\frac{1}{2}$ tons of alum whereas 1 ton of potassium chloride would be expected to produce 6 tons of alum. ²⁵⁶

The potassium chloride was obtained from a lixiviation of kelp ashes by fractional crystallisation. After the sodium salts had crystallized the

supernatant liquid was decanted and from it the crystals of potassium chloride obtained. The partly dried product was the commercial potassium chloride. ²⁵⁷

The ammonium sulphate was obtained from "gas water" from gasworks. ²⁵⁸
Since the gas washings would contain dissolved ammonia but not sulphate, this would at first sight indicate scrubbing of the gas with sulphuric acid - a process still in use. ²⁵⁹

Potassium sulphate was at this later stage obtained from adding sulphuric acid to commercial potassium chloride although it had previously been obtained "from the vitriol makers." ²⁶⁰

By 1862, according to the report of the British Association, meeting of that year, mentioned above, only one plant was producing potassium alum - the others produced the cheaper ammonia alum. ²⁶¹

5) THE PREPARATION AND APPLICATION OF THE ALKALI.

ASHES (1)

The kelp ashes were placed in pits and water poured over them.

After a time, this was drained and more water added. The solution produced called kelp lees was stored. The pit was refilled with water, whereupon the ashes were "turned" to present fresh surfaces to the solvent and the steepings continued until the ashes were exhausted. Dodds records these operations as follow

"Finished steeping our kelp ashes for the Spring season

Lees came as follows

1st time weight	3d	4x do and 1st after turning	3½d
2nd do	2½d	5x do and 2nd do	2
3rd do	2	6x do and 3rd do	1" (262)

It appears that this density control carried out on the solution in the unstirred pits served to inform the operatives both when to "turn" the ashes and when to discard them. The tests prevented the expenditure of water and employee hours on an exhausted "ash" (and also prevented the discarding of soluble solid) which would have resulted in errors^{which} could be cumulative since excess water would cause further dilution of the lees and require more heat in subsequent evaporations.

This controlled system could obviously cope better than a "fixed number of washings" - with the variable composition of the kelp as can be clearly seen in Dodd's account of an unusually rich kelp of which he noted in a letter dated March 1783 that the "lees came off^{at} the amazing weight of 5½d." ²⁶³

The full record is included in the monthly account.

"Memo of the steeping of kelp ashes this season

1st time steeped lees came out at	5½d	5th time and 1st after turning	3½d
2nd	"	6th	2
3rd	"	7th	1½
4th	"	8th	1 (264)

In this case, 8 washings were required as opposed to 6 above or, in other words, the richer kelp required 33% more water. The total volume of lees collected showed in both cases a density between 2d and 3d or a total dissolved solid of about 30 grams per litre.

With the potassium salts representing^{ing} about 30% of the dry weight of the ashes and about 60% of the total dissolved solids we could expect a concentration of potassium "salts" of about 20 grams per litre. ²⁶⁵ The potassium ion concentration would be somewhat less.

71

(2) From Dodd's comments above, we are led to expect that he assessed the soapers ashes as, weight for weight, twice as effective as kelp, although there is no record of any "steepings" of the ashes (For Winter's analysis, see page 113).

(3) The use of "sandibar" or sandiver is more mysterious still. Dodds did not have any faith in it, and Knapp's analyses indicate that it contained only traces of potash, although the written conclusion indicated a possible potassium concentration of appreciable size.

(4) The technique involved in the use of potashes and barilla is nowhere mentioned, however, a record exists of the purchase of a "small cask" of Pearl Ashes, and in a letter of Dodds, he is found quoting at second hand that Lord Mulgrave's agents have reported "that the Spanish war (is) preventing them from having the Barilla Ashes as before" which lead to Lord Mulgrave's works using kelp.

(5) Muriate and Sulphate of Potash

These were relatively pure crystalline salts compared to the more variable potashes. The most important consideration raised here is their application as solids direct to the alum liquor. As Usher outlined above in his letters to Losh, both methods were considered - solid and lees - but the alum maker preferred to use the dry salt and it was for this reason that the presence of insoluble matter could not be tolerated.

An indication of the use of the dry salt is found in a report of a series of investigations of 1810 wherein is described the basis of drawing up a table to assist the alum maker in weighing out the "correct" quantities required. The table ~~required~~ related the mean depth of the pans to the quantity of dry salt to be added - mean depth since the pans sloped at the bottom to facilitate the removal of the contents.

In the words of the author of this report

"The table is constructed for the clarifying pans in the old house for to guide the alum maker they are constructed from 20-24" mean depth ascending $\frac{1}{4}$ " from 20-24" and are calculated on the principle that $16\frac{1}{2}$ lbs of muriate is to be added to every 100 galls of raw liquor at 12d and as the alum maker cannot always have the pan precisely the same fullness, room is given him by the table - for example, if the mean depth of a pan is 21", there is $597\frac{1}{2}$ galls in it and will take 97 lbs 7 ozs of muriate, should

another pan be fuller suppose $22\frac{1}{2}$ " mean depth of liquor the quantity in gallons will be 6326 and will require 104 lbs 6 ozs muriate. (270)

The addition of dry salt raised the density of the liquor. On 26th Feb. 1810, this rise was assessed at $\frac{3}{4}$ cwt. (271) The addition of kelp lees, as noted above, reduced the density of the liquor (see page 32). Thus, the use of the dry salt would lead to a lower fuel cost during the evaporation stages and when the mothers were recycled. According to Ure, and the other commentators, the concentration stage preceded the addition of the alkali but in this investigation of 1810, a different practice ~~was~~ that of adding ~~the~~ alkali to the pans before heating ~~seems~~ indicated.

The investigator notes that 7509 galls of clarified liquor were dosed with alkali giving a final weight of $13\frac{1}{2}$ cwt. This was run into 18 pans and boiled up to $21\frac{1}{2}$ cwt and after being left for 3 hours with "fires withdrawn and furnace doors open" was siphoned into the coolers where the final quantity of liquor was 4162 gallons and he notes that 3347 galls were lost by evaporation during the boiling operation which took $20\frac{1}{2}$ hours.

These results seem to bear out the need to avoid too great a dilution of the solutions and the cost of evaporating 3347 galls or 15 tons of water in terms of coal consumption alone must have been sufficiently great at the optimum weights for the solution. The cost of such quantities of coal must have increased enormously as the demand for coal mushroomed during the course of the nineteenth century and served to reduce the profitability and eventually the viability of the process. It is worth noting here that the basis of all Peter Spence's early patents was to produce a liquor subsequent to calcination of the shales "so as to be able to crystallise without any supplementary evaporation. and it was the final success of the Spence process coupled with the geographical proximity of his works to the consumers of the alum which led to the final demise of the North Yorkshire works and ultimately the Scottish works. 272

WASHING AND RECRYSTALLISATION

There is little information in the records on the technique of washing and recrystallisation of the alum "powder" produced in the last process.

It is noted in the above investigation that the crystals produced in the coolers were of fine hard clear alum and that the "mothers" - liquor drained off weighed 19 cwts - a drop of 2 cwt from the liquor when boiled up. ²⁷³

In the use of furnaces for clarifying or concentration and during roaching or recrystallisation, one finds a dearth of detail in the manuscripts.

However, the secondary sources provide some useful information at second hand which give some clarification.

LIQUORS

Ure, in his supplemental work "Recent Improvements in Arts, Manufacture and Mines" ²⁷⁴ quotes Maurice Scamlon - described as having superintended for some time the alum works of Lord Mulgrave - as the source of this list of liquors found in use on the alum works. Although we have encountered some of these liquors previously, repetition serves to reinforce the information contained in the manuscripts and relate the two final processes to the previous ones.

We have already met

Raw Liquor weighing 9-10d and produced by steeping the calcined shale in "water"

Clarified Liquor weighing 10-11d made by boiling the raw liquor in lead pans and leaving it to stand until clear.

However, in Scamlon's account, the liquor to which the alkali is added is a clarified liquor boiled down to 25-30d. The potash is then added and the solution run into coolers to crystallise and the liquor remaining pumped away. The liquor which corresponds to the "mothers" of 19d above is called the Alum Mother Liquor.

The crystals were then washed twice in water and the Alum Washing collected. The first washing was assessed at a weight of 4d and the second at 2½d.

Two other liquors are mentioned which are not of direct relevance here; the so-called Concentrated Liquor could be obtained by boiling down the clarified liquor to a weight of 20d. This was, according to Scamlon, kept for the purpose of testing the alkali.

The Salt Mother was the liquor remaining after the alum mothers were boiled down to a "crystallising point". The crystals produced were Rough Epsoms, a byproduct of alum making which is considered with Slam below.

FURNACES

The heating of liquors in North Yorkshire was carried out by direct heat applied to the bottom. Although the use of surface evaporation by means of a form of reverbatory furnace was the norm in Scotland, Watson comments that no advantage had been shown when this technique was used in England. ¹⁷⁵

A method which seems to combine both techniques was described as being used in Yorkshire around 1815 by Robertson Buchanan in his book "A Treatise on the economy of fuel and management of heat." published in Glasgow in that year.

Buchanan notes that (176)

"An important improvement has lately been introduced ... by means of which ... (there is) ... a great saving of fuel ... the process is much facilitated and its rapidity greatly increased."

whereby the simple means of placing a 4" pipe with

"it open mouth a few inches above the surface of the liquid ... (from where it) ... descends nearly to the bottom of the boiler... (and) ... out of the side into a short flue"

this

"communication between the surface of the liquor and the chimney ... which ... (has) ... a strong draught, answer the double purpose of lessening the pressure of the atmosphere and carrying off the steam as fast as it rises to the surface."

ROACHING

This final step in the process produced the finished article - saleable alum crystals. Once more, it is difficult to obtain process details in the records although many items exist showing the amounts of alum roached (page 75) comparative figures for alum production (page 95-b) and an attempt to quantify the relationship between the mass of alum produced and the raw materials used. ¹⁷⁷

However, this fairly simple recrystallisation in which the alum powder was dissolved in the minimum quantity of water required to dissolve it at the boiling point of the saturated solution produced is described fully in the other account. ⁵

Album	Reached	at	Bottle	album	Notes
Jan 1791	4	3-6	4	4	May 1792
9	8	8	8	8	6
12	10	10	12	10	12
16	14	14	16	14	16
19	17	17	19	17	19
23	21	21	23	21	23
26	24	24	26	24	26
30	28	28	30	28	30
Jan 1790	2	1	2	1	June 1792
9	7	7	9	7	8
13	11	11	13	11	13
16	14	14	16	14	16
20	18	18	20	18	20
23	21	21	23	21	23
27	25	25	27	25	27
30	28	28	30	28	30
Feb 1790	1	1	2	1	July 1792
5	4	4	6	4	5
9	8	8	9	8	9
13	11	11	13	11	13
17	15	15	16	15	17
20	18	18	20	18	20
24	22	22	27	25	24
27	25	25	30	28	27
Mar 1790	3	2	4	3	Aug 1792
7	6	6	7	6	8
10	9	9	11	9	10
13	12	12	14	12	13
17	15	15	18	16	17
20	18	18	21	19	20
24	22	22	25	23	24
27	25	25	28	26	27
31	29	29	31	29	31
Apr 1790	4	3	5	4	Sept 1792
8	7	7	9	7	8
11	10	10	12	10	11
15	14	14	15	14	15
18	17	17	18	17	18
21	20	20	21	20	21
24	23	23	25	24	24
27	26	26	28	27	27
31	30	30	31	30	31
May 1790	5	4	6	5	Oct 1792
9	8	8	10	8	9
12	11	11	13	11	12
15	14	14	16	14	15
18	17	17	19	17	18
21	20	20	22	20	21
24	23	23	25	23	24
27	26	26	28	26	27
31	30	30	31	30	31
June 1790	6	5	7	6	Nov 1792
10	9	9	11	9	10
13	12	12	14	12	13
16	15	15	17	15	16
19	18	18	20	18	19
22	21	21	23	21	22
25	24	24	26	24	25
28	27	27	29	27	28
31	30	30	31	30	31
July 1790	7	6	8	7	Dec 1792
11	10	10	12	10	11
14	13	13	15	13	14
17	16	16	18	16	17
20	19	19	21	19	20
23	22	22	24	22	23
26	25	25	27	25	26
29	28	28	30	28	29
31	30	30	31	30	31
Aug 1790	8	7	9	8	Jan 1793
12	11	11	13	11	12
15	14	14	16	14	15
18	17	17	19	17	18
21	20	20	22	20	21
24	23	23	25	23	24
27	26	26	28	26	27
31	30	30	31	30	31
Sept 1790	9	8	10	9	Feb 1793
13	12	12	14	12	13
16	15	15	17	15	16
19	18	18	20	18	19
22	21	21	23	21	22
25	24	24	26	24	25
28	27	27	29	27	28
31	30	30	31	30	31
Oct 1790	10	9	11	10	Mar 1793
14	13	13	15	13	14
17	16	16	18	16	17
20	19	19	21	19	20
23	22	22	24	22	23
26	25	25	27	25	26
29	28	28	30	28	29
31	30	30	31	30	31
Nov 1790	11	10	12	11	Apr 1793
15	14	14	16	14	15
18	17	17	19	17	18
21	20	20	22	20	21
24	23	23	25	23	24
27	26	26	28	26	27
31	30	30	31	30	31
Dec 1790	12	11	13	12	May 1793
16	15	15	17	15	16
19	18	18	20	18	19
22	21	21	23	21	22
25	24	24	26	24	25
28	27	27	29	27	28
31	30	30	31	30	31

Watson explained the development of ~~leaded~~ lead lined casks as being due to the improved appearance of the crystals and the greater ease of their removal from the metal surface.²⁷⁸

The liquor left in the roaching cask after recrystallisation is called 279 Turn Liquor and is recycled to join the Alum Mother^s in 280 a further precipitation step.

CONTEMPORARY APPRECIATION OF THE PARTICIPANTS AS SCIENTISTS.

Before completing this account-based on the manuscripts of the participants themselves, all that remains is to discuss certain matters which although important, do not involve the control of alum making - it is worth noting that Winter above, whilst bemoaning the attitude where

"Every suggested improvement is considered as an innovation by the illiterate ... (and it is) ... more easy to remove mountains than long established prejudices." (280)

remarks that

"The alum works that approach the nearest to the true chemical principles are those of the Right Hon. Lord Dundas and Messrs. Baker & Co."

and he summarizes the ways in which they demonstrate their superiority

"They use no urine in these works - the alum liquor is always clarified previous to its being used - they use no alkali generally but crystallised muriate ~~muriate~~ of potash - greater economy is observed in the consumption of fuel and the result is a product of alum considerably larger and of ²⁸¹ better quality than can be produced by the works established in the old plan."

Although one may wish to qualify, to some little extent, the views thus expressed, one must conclude that the manuscripts of these two works so fortunately preserved offer ample evidence of the meticulous and rational organisation of the two works.

URE'S ACCOUNT OF 1839

This account by the well-known chemist and compiler, Dr Andrew Ure, (1778-1857) appeared in his "Dictionary of Arts Manufacturers and Mines", published in 1839. ²⁸² This compilation ran through several editions in which it was progressively brought up to date and was popular enough to be published in further editions after Ure's death, e.g. in 1861 there was a new edition, ²⁸³ edited by Robert Hunt.

As an account, it is much more crisp and businesslike than those previously mentioned - as befits a dictionary entry. Although he no doubt uses previous articles (e.g. he gives the same figures as Wilson for the production of alum from schist - 1 ton from 130 tons schist - and also for the size of the heaps) he is far more aware of the technical aspects of the flow of materials and in his "Improvements" published 1845 ²⁸⁴ he demonstrates that he has been in contact with at least one of the Plant Managers. For this reason, we may treat the account as independent of the others.

Ure breaks down the process into six clear sections which he describes as ²⁸⁵

- | | |
|---|-------------------|
| 1. The preparation of the alum slate | CALCINING |
| 2. The lixiviation of the slate | LEACHING |
| 3. The evaporation of the lixivium | CONCENTRATING |
| 4. The addition of the alkaline ingredients
(or the precipitation of the alum) | PRECIPITATION |
| 5. The washing of the Aluminium salt | WASHING |
| 6. The crystallisation | RECRYSTALLISATION |

1. CALCINING

Ure notes the fact that slates low in bitumen or coal need to be interstratified with fuel - small coal or brushwood but that if the rock is high in combustible matter, only the first layer of fuel is required which "may be laid over the first bed of the bitumenous schist."

The heap is built up layer by layer as described above and Ure remarks that the excessive heat will cause a waste of sulphur and sulphuric acid and suggests a pyramidal heap plastered over. He also commends the Hurllet system

where the heaps were only a few feet high but covered a wider horizontal area.

It is unfortunate that Ure does not give a measure of this area but if a "few feet" (height) were as much as ten feet, then on Ure's figure of heaps at Whitby of 90 to 100 feet high by 200 feet square, an equivalent heap would be 600 feet square to fit the Hurlet model and the geography of the Whitby sites restrict the possibility of such large surfaces being available except on the exposed cliff tops.

He points out that the slower

"the combustion, the richer the roasted ore will be in sulphate of alumina"

and gives several instances of the mishaps due to excessive or over-rapid combustion e.g. iron sulphide combining with the silex to form a slag or sulphur driven off into the atmosphere.

The ideal result is a light reddish ash covering a porous heap of about half its original bulk. In order to obtain a fairly "continuous" supply of prepared slate, a "sufficient number or extent" of heaps should be laid - a recognition of the divisions of the heap which contrasts with his original criticism of the large heaps.

"The beds are known to be sufficiently decomposed by the efflorescence of the salt which appears upon the stones, from the strong aluminous taste of the ashes and from the appropriate chemical test of lixiviating an aliquot average portion of the mass and seeing how much alum it will yield to solution of muriate or sulphate of potash."

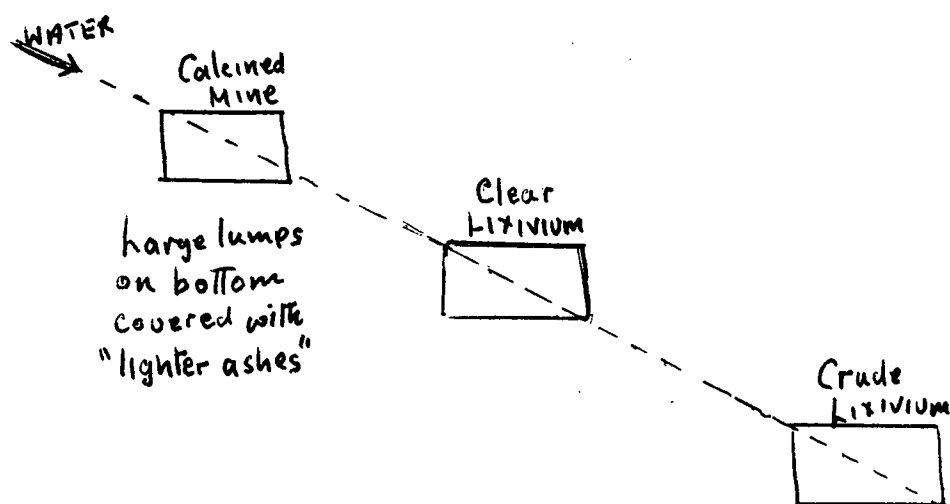
2. LEACHING

Ure advises stone built cisterns - since wood is decomposed and may soon need repairs - which should be built near the heaps to save transport and

"arranged so that the solutions from the higher cisterns may spontaneously flow into the latter".

This "advice" is descriptive of the pre-existing system in use at Boulby and serves to remind us that in all accounts except the manuscripts of Boulby and Loftus, the analytical research of Wilson and the archeological account of the Teesside Industrial Archeology Society we are dealing with second hand information.

The description list the layout of the tanks on a "sloping terrace" as follows:



"In order to save evaporation, it is always requisite to strengthen weak leys by employing them instead of water for fresh portions of calcined schist. Upon the ingenious disposition and form of these lixiviating cisterns, much of the economy and success of an alum works depends. The hydrometer should be always used to determine the degree of concentration which the 'solution acquires'."

Here, there is no description of counter current flow only an assumption of craft skill.

The required density is in the specific gravity range 1.09 - 1.15 and can always be achieved by

"pumping up the weaker solutions on to fresh calcined mine."

The final liquor is removed and allowed to settle to precipitate

"sulphate of lime, the oxide of iron and the earths".

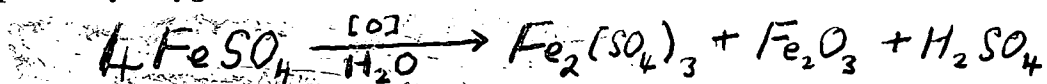
A chemical recommendation then follows.

"It is of advantage to leave the liquor exposed for some time whereby the green vitriol may pass into a persulphate of iron with the deposition of some oxide while the liberated acid may combine with some of the clay present so as to increase the quantity of sulphate of alumina. The manufacture of alum is the more *imperfect* as the quantity of sulphate of iron left undecomposed is greater and therefore every expedient ought to be tried to convert the sulphate of iron into sulphate of alumina."

Briefly in modern terms the suggested mechanism can be written:

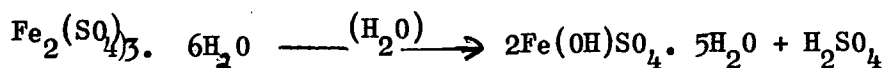
iron (ii) sulphate iron (iii) sulphate + iron (iii) oxide +
hydrogen ion

A clearer picture is that the iron (ii) sulphate is oxidised to iron (iii) sulphate by oxygen in the air.



The iron (iii) sulphate will form a basic sulphate and an acid solution on

hydrolysis.



The complete aerial oxidation of iron (ii) sulphate and the gradual darkening due to the formation of colloidal iron (iii) oxide takes weeks. During this time the subsequent hydrolysis of the iron (iii) sulphate liberates acid to combine with aluminium (iii) ions in the aluminium silicates present in the clays.

3. CONCENTRATING

Ure separates the descriptions for Scotland and for North Yorkshire.

In the Whitby practice, he describes concentration of the liquors in lead pans of dimension 10' long 4'9" and of depth 2'9" at one end and 2'2" at the other, this discrepancy explained as providing a slope to facilitate removal of the contents. The pans are supported by bars and heated from beneath.

In the Scottish practice, which Ure appears to favour, there was surface evaporation of the liquor in a stone tank of dimensions 30' - 40' long, 4'6" deep and 2' - 3' deep covered with a brickwork arch. A fire is set up at one end and a "lofty chimney" at the other. The liquor is evaporated by the hot fumes in their passage from fire to chimney and the tank is replenished by gravity feed. When the density is sufficient, the liquor is transferred to the "proper lead boilers".

Some economy of heat was achieved by the occasional practice of replacing the arched roof of the reverberatory furnace by a flat metal pan of crude liquor which then feeds the lower pan of hot liquor for evaporation.

This stage of the process produces liquor in the specific gravity range of 1.4 - 1.5

"being a saturated solution of the saline matters present".

The specific gravity requirement is related by Ure to the relative proportions of iron and aluminium sulphates. If this ratio is 1:2 a gravity of 1.25 is sufficient but if 2:1 a gravity of 1.4 may be needed to allow the iron (ii) sulphate to precipitate and be removed.

Mother liquors (see below) are added to the crude liquor in the pans to recycle unused aluminium sulphate from previous recrystallisations.

4. PRECIPITATION

Use generalises that the concentration process should not as a rule have been 'pushed' to the point when on cooling, magnesium or iron sulphates crystallise, as this could also lose aluminium from the solution. This indicates that the comment above on specific gravities refer to unusual circumstances (see below), since in this section, the rule enunciated is that the alum be precipitated first as small crystals so as to leave the other species in solution to be recovered where desired.

To achieve precipitation the liquor is transferred to a new tank and

"the proper quantity of sulphate or muriate of potash or impure sulphate or carbonate of ammonia added to it".

Ure gives indications as to the correct quantities for example potassium sulphate will be 18% of the final alum and this quantity or equivalent of the other salts should be added. This vague indication is clarified later where he points out that the added quantity of alkaline salts depends on the proportion of potash or ammonia in the "alkali" and the proportions of aluminium sulphate in the liquor and

"must be ascertained for each large quantity of product by a preliminary experiment in a precipitation glass. Here an aliquot measure of the aluminous liquor being taken, the liquid precipitant must be added in successive portions, as long as it causes any cloud, when the quantity added will be indicated by the graduation of the vessel."

The precipitation being complete the mother liquor is removed and a complete drainage of mother liquor is advisable. As was mentioned above this is recycled to join the raw liquor in the concentration stage.

This recycling is argued to balance the errors arising from the use of the analysis result on the large scale process since excess alkali at one stage will be taken up by excess aluminium in the mothers of a previous batch.

The mother liquor which has a specific gravity of 1.4 is described as a saturated mixture of iron (II) sulphate, iron (III) sulphate and "in some areas" magnesium sulphate. This latter must apply to Whitby where production of the

by-product Epsom Salts was undertaken.

Alternatively the mother liquor could consist of the chlorides of the above species if "muriate of potash" were used and if "s~~o~~ap salts" were the alkali would contain in addition sodium chloride.

Although Ure indicates a preference for the use of the sulphate he points to an advantage in the use of the chloride since it is three times more soluble than the sulphate (which must be used with it) and converts the iron sulphate to iron chloride which is very soluble and less likely to precipitate with the alum.

If a great amount of iron salts is present, he again recommends prior precipitation of the iron but this method requires more plant and man hours and should only be used if it is essential since aluminium co-precipitates with the iron which gives a dull copperas compared to that produced by the evaporation of the mother liquor and this latter evaporation is necessary on occasion to free it of the iron content.

5. WASHING

The small crystals produced will be brown due to the presence of iron which can be removed by water washing in very cold water. Two washes will suffice and the use of least water and good drainage of the washings improves the process (alum is only soluble to 1/16 part by weight or 6%). The second washings are suitable for a first washing of a subsequent batch and on recovery, the washings are added to the crude liquor.

6. RECRYSTALLISATION

"The washed alum is put into a level pan with just enough water to dissolve it out at a boiling heat and dissolved by stirring and heating. The solution is run into the roaching casks of dimensions 5' high 3' wide in the middle. The hoops must be easily removed. It is then allowed to cool and crystals form on the ends and inside the cask walls forming a solid appearing mass. After ten days, the hoops are removed, the staves stripped off and the mass of alum pierced and the 'mother water' recycled to the boiling pans with the next batch of alum powder."

The alum is broken up and allowed to dry and packed for shipment.

The final iron content is about 1% for which he quotes Thenard and Rouard. 285a

AMMONIA ALUM

Ure adds a note on the use of ammonium salts as alkali which is only briefly mentioned in the running account and "putrid urine" is mentioned as a potential source of ammonia. He considers the potash and ammonia alums as similar in properties and gives this analysis to show similarity in composition.

<u>POTASH ALUM</u>		<u>AMMONIA ALUM</u>	
Sulphate of potash	18.34	Sulphate of ammonia	12.68
Sulphate of Alumina	36.20	Sulphate of Alumina	38.64
Water	<u>45.46</u>	Water	<u>48.48</u>
	<u>100.00</u>		<u>100.00</u>

They can be distinguished from each other by the action of quicklime which liberates ammonia from the ammonium alums.

KNAPP'S ACCOUNT

The account of Professor Friedrich Ludwig Knapp of Giessen translated by Drs Ronalds and Richardson presents a further chemical account but one must take care since Professor Knapp's account, although describing English practice, is rooted in the German practice of the time. Some of the comments on British practice are the annotations of the interpreters of whom Dr Richardson was a consulting chemist on Tyneside.²⁸⁷

Alums are described as a collection of double salts which can be represented by

"the general formula $MO, RO_3 + M_2O_3, 3RO_3 + 24aq$ in which R represents the radical of the acid and M the metallic salt base"

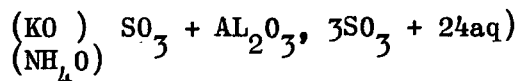
"The acid can be chromic acid CrO_3 or sulphuric acid SO_3 ."

MO can be potash (KO) soda (NaO) oxide of ammonia (NH_4O).

M_2O_3 can be iron oxide (Fe_2O_3) aluminium oxide (Al_2O_3) or chromium oxide (Cr_2O_3)."

The different groups may replace each other to give mixed alums but the crystal will always contain "24 equivalents of water of crystallisation."

Commercially there were only two in use, potash alumina alum or ammonia alum or a mixture.



Their use as Ure points out earlier - is a result of the alumina in them "as the sulphate of potash and water of crystallisation are in themselves superfluous"

but alum is the cheap way of preparing an aluminium salt since aluminium sulphate is soluble in 2 parts of cold water - therefore difficult to separate from iron sulphate.

Whereas 1 part alum crystals at 12.5°C (55°F) soluble in 13.3 parts water
but at 87.4°C (190°F) soluble in 0.6 parts water.

Knapp goes on to describe the extraction of "Native alum" but this would take us beyond what is previously described since the process is different to that of manufacturing alum from alum shale.

Analyses are given of many of the German alum shale^s as well as those of Whitby and Campsie - the Whitby analysis is by Dr Richardson, one of the two translations - which are reproduced here.

	<u>WHITBY</u>			<u>CAMPSIE</u>		
	<u>Top Rock</u>	<u>Bottom Rock</u>		<u>Top Rock</u>	<u>Top Rock</u>	<u>Bottom Rock</u>
Sulphuret of iron	4.20	8.50	Sulphur	22.36	23.44 Pyrite	9.63
			Iron	18.16	15.04	
Silicon	52.25	51.16		15.4	75.4	0.47
Protoxide of iron	8.49	6.11		-	-	2.18
Alumina	18.75	18.30		11.35	11.64	18.91
Lime	1.25	2.15		1.40	2.22	0.4
Magnesium	0.91	0.90		0.50	32	2.17
Oxide Mangan	tr	tr		0.15		8.55
Sulphuric acid	1.37	2.50				6.05

Potash	0.13	tr			1.26
Soda	0.20	tr			0.21
Chlorine	tr	tr			
Coal	4.97	8.29	Carbon loss 29.78	Carbon 28.80	
					8.51
					aq 8.54
Water	2.88	2.00		loss 3.13	0.59
	<u>95.40</u>	<u>91.91</u>	<u>100.00</u>	<u>99.99</u>	<u>100.00</u>

Description of the process is divided up in a similar manner to Ure's account.

ROASTING OR USTALUTION

Where ores are not oxidised by contact which process produces sufficient heat to

"fire spontaneously the carbonaceous parts"

the ore

"must be disintegrated by roasting in order to obtain a free passage of air into the interior of the mass."

The description of heap formation is the same as that described in previous accounts.

The chemical effect of roasting is summarised below. Half the sulphur drives off from the pyrite - partly converted to sulphurous acid partly 'sublimed' on cooler parts of the heap. The "protosulphuret" remaining or, if a low heat, "8/7th sulphuret", later converts to green vitriol.

When the mass reaches red heat aluminium sulphate breaks down - acid is driven off but

"compensated by simultaneous loss of mass by the green vitriol."

Decomposition of heaps of

"from one to several hundred feet in length is slow"

roasting requires 10-12 months (18-24?) and then a further 6-8 weeks decomposition.

"The state of the heap is judged by extracting portions of the ore or by the taste and general appearance of the decomposed mass."

LIXIVIATION

The use of lead lined wooden tanks and walled cisterns over a "false bottom" made by beams covered with straw and brushwood and finally wooden boards is described.

"Ley is first poured upon the one of 20°B (= sp gr 1.157), when this has run off, it answers to 24°B or 25°B and is fit for boiling; a weaker ley of 15°B (= sp.gr.1.113) and subsequently others of 10°B (=sp.gr.1.072) and the weakest of 5°B (=sp.gr.1.034) then follow; and lastly, the whole is washed out with pure water. All the leys that fall short of 24°B or 25°B are poured upon more or less exhausted ones, according to their strength. The movement of solutions can be facilitated by 'arranging the cisterns upon terraces'."

A note in brackets, upon the names of Yorkshire liquors ascribed via Ure to Mr Scanlon, now follows; this would appear to be one of the translators annotations.

The recovered ore may be recycled back to roasting (a) if exhausted to cover the heaps (b) if not fully exhausted to re-expose separately or mixed with fresh one. Previously, an analysis of the

"composition of the residue from the above Campsie ores after calcination and washing out with the alum"

had been given and is possibly descriptive of the efficiency of the roasting process as can be seen here.

Silicon	38.40
Alumina	12.70
Peroxide of iron	20.80
Oxide Manganen	trace
Lime	2.07
Magnesia	2.00
Potash	1.00
Sulphuric acid	10.76
Water	12.27
	<u>100.00</u>

In making the crude liquor, it is inadvisable to allow it to become

saturated in iron or magnesium sulphate where evaporation or temperature rise would cause them to crystallise before required.

"In general, the density indicated by 20°B (=sp.gr.1.15) is not exceeded."

The crude liquor in use at "Gliessen in Neumark" was analysed as follows:

Sulphate of Alumina	11.085	}	29.678
Prolosulphate of iron	9.773		
Sulphate of soda	2.035		
Sulphate of magnesium	1.754		
Sulphate of Manganen	0.174		
Sulphate of potash	0.095		
Sulphate of lime	0.120		
Perchloride of iron	1.872		
Chloride of magnesium	0.334		
Chloride of aluminium	0.419		
Free sulphuric acid	0.563		
Free hydrochloric acid	1.454		
Water			<u>70.322</u>
			<u>100.00</u>

Knapp commenting on then result points out that some ready formed alum

"always accompanies these constituents sometimes potash, sometimes ammonia alum when a red heat has not been employed in the manufacture which decomposes the latter leaving only alumina un-volatilised. To the production of the former the potash naturally contained in the ores assists and still more that which exists in the ash of the wood employed as fuel; the ammonia is attributable to the nitrogen contained in the coal."

The reaction, mentioned by Ure, which occurs when the crude liquor is left for a while ~~Exposed~~ to the air or as Knapp describes it, "clarifying in the large vats" is described as follows:

10 equivalents $\text{FeO}, \text{SO}_3 = 10\text{Fe} + 100 + 10\text{SO}_3$ which absorbs from the air

5 equivalents oxygen = $\frac{50}{\text{---}}$

$10\text{Fe} + 150 + 10\text{SO}_3$ and a basic salt.

$2 \text{Fe}_2\text{O}_3, \text{SO}_3 = 4\text{Fe} + 60 + \text{SO}_3$ is produced and precipitated whilst

3 equivalents of $\text{Fe}_2\text{O}_3, 3\text{SO}_3 = 6\text{Fe} + 90 + 9\text{SO}_3$ or an acid persalt remains in

solution.

He surmises that the acid salt has been overlooked in the Gliessen analysis or else may be accounted for in one of the species enumerated - in any case in the dilution of the crude liquor nearly the whole of the iron oxide is precipitated.

BOILING

"The further treatment of the leys depends on the quantity of green vitriol it contains and in most cases, there is quite as much or more of this than of alum. The ley is then used for the production of both salts and alum and vitriol are generally carried on conjointly; but the process of separating the two salts by crystallisation varies much in different manufactures."

A liquor containing a high proportion of iron is "evaporated in pans" into which old iron has been thrown. The persalt formed by the action of the air is thus partly precipitated as a basic salt, one portion of the acid entering into combination with a fresh portion of iron with

"the evolution of hydrogen gas and is again partly reduced to a salt of the protoxide which prevents the decomposition of the green vitriol, and crystallises in large crystals from the solution. In order to form more points of attachment for the crystals and facilitate their removal, the workmen are in the habit of hanging peeled sticks and branches ... in the solution. The mother ley, of course, contains the whole of the sulphate of alumina and is boiled for alum."

A footnote (by translations^{ns}?) remarks that the "basic salt" is precipitated without metallic iron being needed since "dilute solutions of persulphate of iron ($\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3$) are decomposed by heat alone and a basic salt ($\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$) is precipitated."

When the iron sulphate is not "in excess", the alum is precipitated first.

"The [clarified liquor] is pumped into the evaporating pans. If these are composed of tinned iron, they become attacked by the sulphate of alumina and the ley, with the evolution of hydrogen and basic sulphate of alumina, is precipitated when the action, which is similar to that of an acid is not prevented by the addition of the basic mud before mentioned. Notwithstanding this, the sediment frequently gets burnt on to the bottom and causes difficulty and damage, particularly when cast iron or leaden pans are employed which are not otherwise affected but the former of which is brittle and the latter too easily melted by the heat. To prevent this metal evaporating pans are now almost universally discarded and the flame is carried over the surface of the liquid instead of below the pan."

There follows a description of a furnace similar to that described by Ure above. It is worth quoting the full passage as it indicates rationalisation upon scientific knowledge but is insufficiently implied. The effect of the sediment in insulating the solution from the heat and thus concentrating it in the pan metal must be taken as understood since the effect

"of a melted pan is stated. However, the effect of displacement of Alumina by tinned iron pans is not transferable to lead pans so one must look elsewhere for the sediment."

The "basic mud before mentioned" is a

"kind of basic alum i.e. an insoluble salt which is deficient in a certain quantity of sulphuric acid to render it neutral alum".

This was also briefly mentioned by Ure as a product of the final stage of the process.

As evaporation proceeds, the pans are replenished with fresh liquor or the "mother liquor" from earlier batches until the gravity of the concentrate becomes 42°B (sec. grav = 1.40).

"In the meantime, a copious sediment is deposited from the ley, consisting of a large proportion of basic sulphate of iron (produced by a continuous decomposition of the copperas and neutral persulphates of iron) of gypsum and other salts which render it necessary to clear the liquor in the cooling vats. Whatever the composition of the liquor may be, it must never be so far evaporated as to deposit salt by cooling in the vessels appropriated to the production of the flour. Everything must remain in solution after cooling and the liquor must be perfectly clear."

PRECIPITATION^{ON} OF THE POWDER

This is the first precipitation step where

"the sulphate of alumina is combined with potash or ammonia (the 'flux'

or precipitating substance)."

The precipitating is due to the low solubility of the alum in the cold mixture and is thrown down in "very small crystals of flour".

The solubilities are quoted as:

9.25 parts	}	dissolves in 100 parts water for	{	Potash alum
9.16 parts				Ammonia alum
46 parts				Soda alum

which precludes soda as a suitable precipitating agent.

Theory indicates that:

100 parts of alumina requires 50.9 parts K_2SO_4 or 47.8 parts $(NH_4)_2SO_4$.

"The precipitating substance cannot be employed in the dry state, as the point of saturation would not then be distinctly known ... on the other hand, perfectly saturated liquor is only used that too much water may not be introduced into the flour cisterns and the largest produce of meal may be obtained."

On the basis of an analysis of the liquor as being saturated and containing in each 100g. water 33.2g. anhydrous iron (ii) sulphate and 33.5g anhydrous aluminium sulphate, Knapp predicts that the said 100 parts water will require for precipitation

- a) 17.1 parts potassium sulphate dissolved in 66 parts boiling water producing 96 parts alum in 166 parts water which on cooling leaves 16 parts in solution giving not less than 80 parts alum
- b) 14.5 parts potassium chloride dissolved in 26.2 parts boiling water producing 96.5 parts alum in 126.2 parts water which on cooling leaves 12 parts in solution giving not less than 84.5 parts of alum.

If used cold (10°) the potassium chloride requires 46 parts water giving a total of 146 parts water which will hold back 13.8 parts alum precipitating 84 parts alum.

Knapp deduces that there is little difference in the two cases. However, because less chloride is required and it can be used cold, he argues that its use is preferable.

In the case of ammonia alum, the solubility of ammonia^{um} sulphate is given as similar to that of potassium chloride and to use the above basis 15.8 parts

ammonium sulphate (dissolve in 31.6 parts boiling water) producing 87.8 parts alum (in 131.6 parts water) which on cooling retains 10.6 parts alum precipitating 77 parts. However, weight for weight, ammonia alum is 95.6% of potash alum.

The sources of potassium sulphate are given as:

- a) secondary product in the nitric acid manufacture.
- b) from the burners of the vitrol chambers on the old plan of manufacture.
- c) purification of potashes.

Knapp claims that it is found in the form of bisulphate ($K_2O \cdot 2SO_3$) which should be converted to the neutral salt $K_2O \cdot SO_3$. Potashes should not be used as a precipitant unless free acid is present since they precipitate, to some degree, a basic alum (produced also during evaporation but can be dissolved by bisulphate of potash.)

He further feels that purifying potash and alum production should be carried on side by side to mutual advantage.

Further advantages of using potassium chloride as precipitant is that manganese and iron (II) and iron (III) sulphate are converted into chloride which are delequescient and easier to remove than iron (II) sulphate.

If iron (II) sulphate is present potassium sulphate will produce a basic iron alum, slightly soluble, which precipitates as a yellow powder contaminating the alum.

However, excess of potassium chloride would convert aluminium sulphate to its chloride which is

"the reason the nature of the ley must be investigated before every operation with a view to determine the precise amount of chloride of potassium that is required to be added."

However, the required amount will "seldom or never" encounter enough iron sulphates in the liquor to convert fully into potassium sulphate. The test seems similar to Ure but more modern terminology is used.

"... a saturated boiling solution of the precipitating salt is added from a graduated burette under constant agitation to a measured quantity of the liquor as long as the flour which falls increases in quantity. The number of measures which have been employed indicate with sufficient accuracy, the amount of solution required to precipitate a given volume of the liquor and the tedious process of weighing is thus obviated. If the liquid however is allowed to cool during the operation, a portion of sulphate of potash (on account of its difficult solubility) may be precipitated with the flour and give rise to an error, for this reason, it is advisable to use as the testing liquid the easily soluble sulphate of ammonia of which 1 part is equivalent to 1.32 parts of sulphate of potash or to 1.13 parts of chloride of potassium."

Other sources of potassium chloride are mentioned as the "soap boilers waste" and "sandiver", from the glass houses, the composition of which is given as

	German Plate	Crystal	Bottle
Water	1.65	0.10	1.00
Sulphate of soda	83.32	90.51	55.92
Sulphate of lime	10.35	6.00	25.11
Chloride of soda	"	"	"
Carbonate of soda	tr	"	"
Potash	"	"	tr
Insoluble matter	3.25	3.35	17.77

Knapp, before quoting the analysis, commented that the salts consisted "chiefly of chloride of potassium (or sodium) and sulphates." The composition tabulated indicates a substance of little use to the alum maker.

Knapp also quotes the use of Kelp in England and Varec or Barolla in France. He states the Kelp is of similar composition to Varec except that it contains metallic iodides.

"Kelp ... can hardly be classed among the varieties of soda; Kelp containing only 2 per cent and Varec no carbonate of soda at all; but consisting of one half chloride of sodium and the other half of about equal parts of chloride of potassium and sulphate of potash ...

"... In Scotland Kelp is a source of potash salts and iodine. When the leys obtained from the ash is evaporated, the soda and potash salts separate one after the other; the latter are used in the alum works, while the mother liquor distilled with sulphuric acid and manganese yield iodine."

A source of ammonium sulphate is from the coal gas works when the gas is absorbed in sulphuric acid and this gives a solution of 80 ounces to the gallon compared to 14 ounces to the gallon from distilling condensed ammoniacal liquor.

WASHING

Knapp does not separate this operation from the preceding one. The flour when produced is thrown onto a slanting board so that the liquor can flow back into the tanks. The crystals are discoloured "brownish yellow" by adhering liquor.

The crystals are stirred with cold water in another tank

"which takes up the mother liquor and a proportion of the crystals corresponding to the temperature and this operation is repeated once or twice. The first two portions of wash-water consist of liquor of medium strength and are added to the evaporating pans, whilst the last portion is used instead of fresh water for the next washing."

CRYSTALLISATION

The crystals are mixed with boiling water or dissolved by steam. Knapp describes the steam process in use in a Moselle works "Volmunster". The product is a saturated solution of 48° to 40°B a specific gravity of 1.485 to 1.515 which is run into the roaching vats and left to crystallise. (The crystals are large - up to 1 lb each).

DISTRIBUTION OF THE PRODUCT

The records of product distribution are remarkably complete and these monthly "Alum Accounts", perhaps due to the operations of the cartel cover all the operating plants in North Yorkshire. Two copies are reproduced as pages ¹⁸⁸ 95 and 96 .

It will be observed that the information in these accounts concerns more than simply the tonnages shipped and destinations; it includes also total production for the month, the number of working pans and the stock remaining.

The mode of transport, although fascinating, does not have any direct influence on the process and is probably worth considering at another time.

Briefly, at Boulby, the alum was lowered through a deep pit or well not far from the cliff face - still visible today although a secure cover is now placed over it - using a horse drawn gin. Details of the apparatus and horse trapping are given in a works inventory ¹⁸⁹ and the replacement of the gin rope is reported in the appropriate monthly account - it lasted about three years. ¹⁹⁰ The casks of alum and slam and later epsoms were stored below the cliffs in store-houses and loaded directly on to ships at the staithes specially built for the purpose. The ships have been described in the short article on "The Alum Ships" by Barton ¹⁹¹ and many comments on their adventures or misadventures can be found in the letters (see excerpt on page 59) which also express anxiety for the safety of cargoes at a time of privateering activity or for the delays caused by adverse weather conditions.

A glance at the destinations of the Alum cargoes serves to remind us that although the shipping was mainly a coastal trade between North Yorkshire and London, other destinations are by no means infrequent and the occasional ship went as far as St Petersburg.

However the main export trade, by ship directly from Yorkshire, was to French ports (the two examples reproduced were chosen to show the diversity of destinations) and this is of interest within the context of the alum process since at the time of the accounts the synthetic alum was being manufactured in France. Plants had been set up by Alban at Javel and Chaptal at Montpellier ¹⁹²

3 458

Memo Account June 1787

Works	Days	all on L. 20 June 1787 Ten Gu.	D. made in June Ten	D. Shipt Ten Gu.	Part Shipt for Ten Gu.	Rem on L. 20 June 1787 Ten Gu.
1. Leach	1	13. 11	15	57	London	31. 11
2. New-Bow	6	12	36	18	D.	30.
3. Little-Brook over boats last 1/2 Mo.	1	97. 10	15	70	Amsterdam	47. 10
4. L. White. Sea	6	85. 10	10	30	London	65. 10
5. Sandstone	9	143	60	30	Spud	90.
6. Millings	9	104	60	40	Rotterdam	30
7. Boulders	9	59. 10	10	93	Venice	34. 15
8. Luffhous	7	14	42	60	London	18.
9. Gunns over boats last 12 Mo.	8	146. 15	15	52	D.	50.
		56. 15		22	Venice	
				84. 15	London	
				40	D.	
				24	Rotterdam in af.	
				55	Venice	
				6	Home brought 2 Mo.	
	18		4. 33	721. 15		397. 6

and Smith assesses that by 1794 the production of synthetic alum at Javel was 35 - 70 + 10³ kilogram per annum (or 35 - 70 metric tons per annum).¹⁹³ Although production grew during the Napoleonic Period this synthetic supply was never able to supply more than a fraction of the needs.¹⁹⁴ Smith points out that "alum" ore extraction was developed until by the end of the Empire France was virtually independent of imports.¹⁹⁵

OPERATIONS OF CARTELS

The operation of a cartel or series of cartels which were agreements between manufacturers to limit and regulate production of alum and therefore prices seems to have been a feature of life in the North Yorkshire industry during the eighteenth century.

An early partner in the Boulby works, Ralph Ward gives evidence of the cartel in operation in his journal for the years 1754-1756 and the Boulby record shows him writing to Wardell on this matter in 1746.¹⁹⁶

On 15 February 1755 he "wrote to Sutton on Allom affair"¹⁹⁷ and met with him and Wardell in Stockton on 2 April 1755 where they "consulted about Allom affair - not settled". On 15 April More, Wardell and Ward discussed the Alum Affair to little purpose (probably at Loftus). 21 April saw Ward discussing the matter with Howlitt and Matthews.

"The Cock" Guisborough provided the venue for a meeting between Wardell of Boulby, More of Loftus and Ward where they discussed the alum affair during or after dinner on 20 November. The same venue saw Wardell, Sutton, More, Heath, Matthews and Mr Edmund Pressick dining and setting "about settling the Alum Affair".

¹⁹⁸ Pickles quotes "Crowthers" History of Lythe for evidence of a "Masters Union" of proprietors to settle production at a total of 3,200 tons per annum but regards this attempt as unsuccessful. He also regards the Alum accounts of 1780-92 mentioned above (pages 95-6) as indicating some attempt to control production.

Clear evidence of a cartel in the 1790s, is the draft found in the Loftus

records and reproduced as pages ²⁹⁹ 99 and 100 . This however seems to be a projected agreement, yet Watson notes the existence of the cartel, and that Boulby held out for a year before joining.

A production limiting cartel within the North Yorkshire works to control the London price of alum seems to indicate that competition from Scotland - just commencing - and Lancashire was non-existent.

Furthermore it seems reasonable to assert that it had no effect on developments in production methods. The phrase is used advisedly since one might expect a cartel to have a negative effect on development even to the point of causing it to cease entirely.

If production could not be increased then a reduction in operating costs had to take place. Examples of this can be found in the above accounts where a better designed furnace was installed to save on heat - i.e. coal; where solid chloride of potash was added to save in labour required for dissolving and in additional heat for evaporation and when Dodds was given recognition for saving costs in a development in the use of Kelp. ^{299a}

The operation of the cartel was important to the economic well-being of the North Yorkshire works and possibly even caused the closure of works whose costs were too high for them to sell at prices charged by the group operating the restrictions but not of significance to the development of the process.

BYE-PRODUCTS

The main bye-products of the process were Epsom Salts and Slam but these were not necessarily produced at the same time.

Prior to 1800 the Boulby records describe the production of slam only.

SLAM

Slam was described by Turton as the "slimy" stuff deposited in the settlers after concentration. ³⁰⁰ Pickles describes it as "a mixture of ferric oxide and silica" which he claims was used by a "bottle glass manufacturer in Whitby" as a raw material. ³⁰¹

The last three decades of the eighteenth century saw the entire Boulby

It is proposed in the first Instance to regulate the
 Proportional Sale of the Quantities made and on
 hand amongst the five Proprietors — and where
 these Quantities are added to a level, according to the
 number of Pans each Proprietor is entitled to work
~~according~~ ^{by} the original agreement — then the proportion
 shall be continued ~~as~~ according to the actual number
 of Pans — and in the event of the Demand for them
 requiring an increase in the Make, each Proprietor
 to put in the same number of Pans, say one, two
 or three each, it is not to exceed the numbers
 in the original agreement —

READING
OFFICE
SECRET
SERVICES

	Worshs	Pans
Lord Mulgrave	2	14
Smith's Duns	1	12
Mr. Cooke	2	12
Mr. Baker	1	8
Mr. Gorman	1	6
		<u>54</u>
if 3 Pans are added by each Proprietor		
The number will be		39
The quantity of Wares made		
at 6 Tons P. Pan a month		2508 a year
The quantity sold in 1791		
including those works which are		
not under the agreement		
Quantity made by Redkey & Co.	392	4618
New Brass	256	4248
in 1791 sold by the five Proprietors in agreement		<u>3870</u>

production of slam - as far as we can tell from the records - being shipped to a Mr Thomas Simpson, merchant of Newcastle upon Tyne described in Whiteheads Directory of 1790 as owning a wholesale oil and colour warehouse in St John's Street, Newcastle.³⁰² In addition it appears he was a colour manufacturer making Prussian Blue.³⁰³

In a letter to Simpson of 15 September 1779 Dodds notes that 46 tons of dry slam had been shipped on the "Mary" under Captain Ovington and remarks that

"I have charged you with two shillings per ton for lowering and shipping the Slam which is more than we pay for the Alum - but the Slam being so bad to deal with - and so pernicious to everything it comes nigh - I cannot conveniently charge you any less." ³⁰⁴

The slam cost £23 per ton and Simpson complained that the cargo was underweight. Dodds, in a letter to Mrs Baker remarked that the slam had been weighed moist and could have lost weight when lying in the store at the foot of the cliffs.³⁰⁵

In a letter to Simpson of 25 September 1779 he then explained how evaporation caused the deficiency of 6 tons in 46 tons or 13 per cent by weight and reacting to a complaint by the above Captain Ovington, Dodds points out that the slam, when wet, is very corrosive to metal work, clothes, etc. but safe when dry and he had told the Captain to keep the slam dry.³⁰⁶

Nonetheless, Dodds was dubious about loading the Baker-Jackson partnership's own ship with slam which he described as not "very eligible".³⁰⁷

The Boulby inventory list^s the slam pans and barrow way³⁰⁸ and records of slam pans³⁰⁹ and building a slam shed³¹⁰ can be found in the accounts. There seems to be a seasonal bias in production of slam - in 1783 slam^{was} lowered (i.e. by the gin) on 20 February, 5 April, 18 April, 5 May, 7 June - or perhaps it is governed by weather as Dodds seems to indicate when he informs Simpson, in March 1781, that "The weather is again favourable for collecting slam".³¹¹

What then, is slam and how was it made? Is it collected in the settlers as Turton indicates above and, if so, what is the purpose of the slam pans - recrystallisation?



The acidic nature of the slam, attested to above, does not bear out Pickles' "analysis" of it as a mixture of oxides and Dodds indicates the specific nature of the acid when in negotiating with Simpson over price and quotas and Boulby supplied \sim 150 tons a year with 358 tons in 1790-1³³ he suggests he may need the slam himself since

"I cannot help telling you I have been thinking we may make copperas here, we have a deal of old iron and much more may be had at an easy rate and I am of opinion the Vitriolic acid of slam will with fire be a proper solvent - I shall thank you for your opinion on this - as I trust you do not make use of Slam for Copperas".³⁴

The slam then contained sulphuric acid or sulphate radical and, if we can trust the technical data here, was too deficient in iron to be pure iron (ii) sulphate or copperas. It could have been iron (iii) sulphate or a mixture of iron (iii) sulphate and aluminium sulphate both of which give acidic solutions. (See page 117). In the early days of the alum works Colwall observed that the liquor could "turn to copperas" when left in the cooler too long or in cold weather. Perhaps this was the allusion in Dodds remark above.

Dodds did not, in fact, make copperas at that time, however, it was made as a by-product at the Hurlet and Campsie plants.³⁵

It seems more likely that Simpson used the slam to make Prussian Blue or potassium ferricferro cyanide $K_4 Fe (Fe (CN)_6)$ which could easily be made by the action of potassium cyanide on an iron (iii) salt.

However Watson in catechetical style describes the manufacture of Prussian Blue as achieved by adding "prussian potash" to iron containing alum liquors. The prussian potash was described as an organic material produced by reducing various natural materials in a metal pot (the full catechism of the topic is reproduced as page 103). This method of manufacture, described by Watson is of more use than the simple chemical preparation noted above in understanding the following entries in the Prussian Blue account at Loftus for 1805.

"Calcining Egg —
 2 lead pans
 Horn shavings
 Dried blood
 Pearl ashes
 Muriatic acid" (316)

EPSOMS

The third by-product was produced by evaporating the mothers after alum extraction until they reached a desired density.³¹⁷ They were then left until crystallisation was complete and the rough crystals were recrystallised.

These rough Epsoms or crude Epsoms contained excess acid and Watson claims that their popularity lay in this property.

If desired pure the rough Epsoms - acidic magnesium sulphate - could be calcined in a reverbatory furnace and magnesian limestone added.

At this later date Watson claims that^{the} principal use of the^{slam} was to recover magnesia.³¹⁸

A visitor to Boulby at about the time the works began to start the final rundown noted on 7 January 1869 that the works produced 700 tons of rough epsoms a year which sold at fifty shillings on Tyneside but could find no orders³¹⁹

THE SCOTTISH PROCESS

We are not concerned here with the sort of background details of partnerships personalia and duration of the plants needed to understand the manuscript accounts of North Yorkshire. Clow's account is fairly complete as regards such details. The first works were opened in the last decade of the eighteenth century with Charles Mackintosh and a Mr Knox as partners.³¹⁰ Although Charles Mackintosh is better known as a chemist—he was a pupil of Dr Black — it is Knox we find "describing" the mine and dictating an account to the Editor of Nicholson's journal in 1807³²¹ and it is Knox who visits Boulby in 1804.³²²

A good contemporary account of the Hurlet process can be found in 'Knapp' and is basically similar to that used in Yorkshire.

The calcining³²³ was accomplished in low heaps as mentioned above; the calcined ore transferred to "stone cisterns" which were filled to eighteen inches above the "false bottom".

The liquor from a previous "steep"^{was} allowed to cover the calcinate and after eight hours^{the} "plug" removed from the bottom and the liquor allowed to flow into a supply cistern. This liquor should have a density of 20°T (1.10) Weaker solutions were now used to leach the burnt ore until the density of the lees drawn off reduces to 12°T (1.06) - these latter solutions^{were} too weak to use in evaporating pans and so were used as washes i.e. to add to fresh batches of ore. The leaching was completed with weaker liquors and water.

The exhausted ore was discharged as waste or used to cover fresh heaps of ore.

The liquors were now run to boilers - long brick cisterns sixty feet by six feet by four feet which could evaporate 4500-5000 gallons of liquor in twenty four hours. The furnace was designed with the furnace at one end and the chimney at the other; the hot furnace gases and to some degree the flames sweep across the surface of the liquor; the furnace was fired for eight days while liquor was added until the last night when the recycled mother liquor was added. The liquor was allowed to settle for at least twelve hours.

A sample of the liquor was tested with potassium chloride to judge the quantity of this salt required to precipitate the alum.

The required amount of potassium chloride was added to the cooler and the liquor at 60°T run in. The liquor in the tank was then agitated and left for four or five days and the "mothers" allowed to drain out.

The "first alum" is found sticking to the sides from where it is removed, washed in tubs with "second mothers", collected in sieves, rinsed and "thrown off" to drain.

The second alum boiler which was a deep stone cistern was partly filled with liquor used in washing the "second" alum. Steam was added until the liquor was almost boiling and washed crystals of alum put in until the liquor reached a density of 60°T. More steam was now added to achieve the highest possible temperature for the liquor which was now allowed to settle for twelve hours. The liquor was run to second coolers where it remained four-five days; the mother liquor at 26°T was drained off and used to wash "first" alums; the "second" alums crystals were now used in the roaching or recrystallisation process.

In roaching the crystals were placed in a closed lead cistern and steam "blown in" until the resultant liquor achieved a density of 96°T. The temperature is raised to 224°F and the liquor left for four-five hours or until the temperature reaches 200°F.

The liquor is then run to the roaching casks - lead lined barrels holding two tons alum - where it remains four-six days. The hoops and staves were then removed and the "sold cask of alum" allowed to stand another two weeks before being pierced.

The run liquor was collected and used to dissolve the "first" alum,

This account shows that the Scottish process is very similar to the Yorkshire process except that the use of steam reduces the cost of evaporation of solution and there appears to be two recrystallisation processes. In addition to density controls - the use of Twaddle's hydrometer was understood

in North Yorkshire as early as 1805 although the traditional "weights" were used - there appears to be some temperature controls associated with the steam induced solution.

This process continued in use until the end of the nineteenth century and was investigated by Wilson - a grandson of one of the original partners - an account of whose researches is summarised below.

THE MANUFACTURE OF SYNTHETIC ALUM

The term "synthetic alum" which I am using to distinguish this chemical route to alum from that which used as raw material the alum shale - is without doubt a complete misnomer. In a sense all alums were synthetic except the "Natural Alum" found at Tolfa, in Italy, and extracted there since the Middle Ages. In all other cases a chemical reaction - usually an oxidation induced by calcination - was required followed by the addition of some species containing the monovalent ions. This is as true in the "synthetic alum" process as in the "alum shale" process. What prompted the use of this term is the somewhat misleading title of the first paper describing a manufacturing process based on this technique in Chaptal's account of the Academic of 1789, entitled - in translation -

"On the method of making alum by the direct combination of its constituent principles".

Chaptal claims that his establishment, then two years old, was showing signs of great activity. In this paper he claims that pure clay which contained "alumina" could be impregnated with vitriol. He preferred to use the vapour (from the chambers perhaps?) since

"this acid is only a mixture of water with the vapour produced by the combustion of saltpetre and sulphur".

The "alum" was removed after the formation of efflorescence, leached, evaporated in lead vessels and crystallised. He notes that he used alkali to assist the formation of the crystals, otherwise, the crystals would neither be "so heavy nor so hard".

Smith notes that the

"synthetic alum process originates from the researches of E F Geoffroy in 1720s which were reported in the Memoirs d'Academie of 1728 under the title "Examens des differentes vitriols avec quelques Essais sur les formations de Vitriol Blanc et d'Alum" where he showed that Alum could be produced by digesting roasted clay with vitriolic acid." 316

Smith goes on to summarise Chaptal's process:

"the roasted clay was pulverised; mixed with sulphuric acid; allowed to stand a few days; heated in an oven for twenty four hours; leached; the solution boiled down, urine or potash added and the solution allowed to crystallise." 317

He claims that Chaptal found this method too expensive in the face of competition from imported alum and that this led him to expose the clay to the "lead chamber" gases.

This process, according to Smith, was regarded as one of the triumphs of chemical manufacture at that time showing the useful application of science to industry. ³²⁸ Although, as mentioned previously, it only supplied a fraction of the total demand for alum, ³²⁹ Singer claims that Chaptal made a fortune from his "improvements" in this process.

Certainly Chaptal thought his process - commenced about 1785 - worth a separate Article - or sub-chapter - of seven pages length, entitled "Of Artificial Alum" in his applied chemistry text of 1807. ³³⁰

In this account he distinguishes between the processes in use at Javelle and at Montpellier. There are other changes compared to the original accounts and so it is worthwhile to again summarise the process in use, - this time - at the turn of the century.

The Javelle process uses the "argil" of Gentilly and is almost identical with that quoted above; sulphuric acid is used and the oven is regulated at 50°-60°B.

A variation on the original process was in use at Montpellier; the crushed "argil" was

"kneaded with half its weight of the product from the combustion of the saltpetre and sulphur employed in the formation of sulphuric acid; it is well known that this residium consists almost entirely of sulphate of potash".

The paste was rolled into balls four inches/^{to}six inches in diameter and roasted in a "potters oven". After this roasting of undeclared duration the balls are put into

"the apartment appropriated for the manufacture of sulphuric acid".

The acid attacks the balls and the action is considered complete after three to four weeks, when they are exposed to the air and subsequently leached etc.

Chaptal describes improvements made by

"M. Berard, my pupil and at present the proprietor of that establishment"

i.e. la Raille, Montpellier. Etienne Berard was involved in the production process since its inception at La Raille, south of Montpellier in 1782. He is described by Smith as a former pupil and laboratory assistant of Chaptal who under his direction produced acid and alum at the plant.

Essentially the improvements are in control or simply a greater care in the various steps. Instead of the chamber gases being used the balls are "sprinkled" with sulphuric acid at 40°, presumably Beaume, equal in "weight" to the argil and the proportions of acid are adjusted "according to the nature of the argil".

The method of M. Curaudeau,—clay and sea water paste, calcined, crushed sulphuric acid added in the exact quantity of one quarter the weight of the calcinate, fumes of hydrogen chloride allowed to "disipate", water added, heat swells solid mass, more water added and finally a solution of "twenty five per cent" potash,—seems designed for small scale use. The step where hydrogen chloride is evolved would indicate a temporary evacuation and the dilution of the mixture by adding water to sulphuric acid could not have been universally popular with the workforce.

Chaptal concludes his 1807 account with a process which he had himself used and which was then being successfully utilised by M. Bouvier. A mixture of clay, potassium nitrate and sulphuric acid in the proportions 100;50;50 (the acid being at 40°— again one assumes Beaume) ~~was~~ distilled to drive off the "nitric acid". The residue can be leached etc to form alum directly. Again one could conclude that this method must be small scale and dependent on the size of the still. Perhaps this is recognised by Chaptal who recommends a clay with a very high proportion of alumina.

The manufacture of artificial alum from "pipe clay" was also carried out in the mid nineteenth century on Tyneside. ³³¹ The clay needed to be carefully examined and was free from iron salts and calcium carbonate. It was dried in

a reverberatory furnace, powdered and sieved. The sulphuric acid was added in the ratio of one hundred parts of clay requiring 42.5 parts of acid of density 1.49 and again the solid material was heated in a reverberatory furnace, "raked out" and the aluminium sulphate^e extracted with hot water at 190°-200°F. Watson here comments that one hot steeping was equivalent to two cold steepings but that in view of the expense incurred in heating the water, this improvement was not practiced in the "older works". The process then followed the usual operations where monovalent ions were added. At this time ammonia liquor was readily available from gasworks and as noted above the usual alum of commerce was by then an ammonia alum.

In 1845 Peter Spence filed his key patent detailing a process in which hot fairly concentrated sulphuric acid was added to hot freshly calcined shale. This was more economic and efficient than a process using cold weathered shale since the action of the acid on the porous³³¹ calcinate would be quicker and more thorough at an elevated temperature. The product could be treated directly with the source of monovalent ions - ammonia liquor from the gasworks - and crystallised to give alum. Providing the temperature of the hot acid could be controlled, the great saving was in the cost of evaporating raw and clarified liquors etc. This, to Spence, was the most important consideration.

Spence, a native of Brechin and one time employee of Dundee Gas Works, set up his plant in Pendleton and contracted with Manchester and Salford Gas Works for their gas liquor over a thirty year period. He used the surplus over and above that needed for alum manufacture to make fertilisers.³³³

Production of twenty tons alum per week had risen to one hundred and ten tons per week in 1860 by which time, according to Singer he had displaced all his British rivals. In 1870 the production was 250 tons per week and by 1882 had reached the order of 100,000 tons per annum.

Although Spence realised, as had many before, that the effective component of alum was, for most processes, the aluminium sulphate, it was not

until the early years of this century that Spence (1919) and others began to make aluminium sulphate itself.³⁹⁴

Hardie and Davidson Pratt claim that there has been no basic change in the alum manufacture since the 1880s.

THE DEVELOPING COMPREHENSION OF THE ALUM PROCESS

The discerning reader of the previous accounts will, no doubt, have found in them - especially those of Ure and Knapp - a considerable chemical understanding of the process. If these are put into their chronological context, then the following synopsis could be said to supplement or be supplemented by them.

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Vauquelin recorded that Bergman had deduced that alum was a triple salt and had discovered that soda and lime, if used in place of potash and ammonia, do not produce a crystallisable alum. He argues that this should have overturned the then current theory that potash, as an alkali, "saturated" any excess acid in the liquor which was, at that time, believed to prevent crystallisation. However Vauquelin claims that Bergman later fell into the "saturation error."

In this paper he reports the synthesis of aluminium sulphate by dissolving alumina in sulphuric acid and evaporating the solution at various dilutions in order to induce crystallisation. The uniform result was a "magma formed of saline plates without consistence or solidity".

However the addition of a few drops of alum solution induced an immediate crystallisation. Sodium Carbonate, lime and barytes had no such effect.

Bergman's result was also confirmed when Vauquelin concluded that:

"Of all the kinds of alum which I had submitted to analysis I did not find one which did not afford sulphate of potash or of ammoniac or frequently both at once".

The conclusions of Vauquelin, whose article was published in English in 1797, are of interest.

1. It was not excess of acid which prevented crystallisation but a "want" of potash and/or ammonia.
2. The sulphate of potash could be used in place of the alkali potash - however he qualifies this by recommending potash against sulphate if the liquors contain iron. He further claims that the sulphate of potash is much better than putrid urine which always contains phosphoric salts whose action is to decompose part of the aluminium sulphate.

To what extent were these ideas taken up by the manufacturers. The dates already given for the introduction of new "alkalis" give an unclear picture. Certainly it can be asserted that the supply of sulphate and muriate of potash which commenced just after the turn of the century was undertaken by William Losh, who could be expected to keep abreast of chemical discovery, especially French. It could also be pointed out that the first plant which we can see buying this material was that of Lord Dundas - chairman at about that time of the committee of the Royal Institution who would no doubt have been informed of the work of Vauquelin.

Against this picture one could recall that the deliveries of putrid urine to Boulby continued until 1807 and that Kelp was available on the Loftus plant at about the same time. Also the abbreviated annual accounts of the Boulby works during this decade refer simply to "alkaline" materials.

Certainly Winter fell into the "alkali" error when he wrote his account of the North Yorkshire process in 1810. He gives an analysis of kelp as 47 per cent soluble salt and 53 per cent charcoal sand and earth. The soluble salts were the chloride, hydroxide and sulphate of sodium. This substance was an inferior "alkali" when compared to "black ashes" which contained only ten per cent insoluble charcoal and earth and the ninety per cent of soluble salts comprised sodium chloride, potassium chloride, sodium sulphate, calcium chloride and magnesium chloride.

It must be immediately apparent on these analyses that as an alkali kelp was superior in that it contained sodium hydroxide yet Winters goes on to compound the error when he states that:

"The muriate and sulphate of potash are the only alkalis that can be used to advantage in the composition of alum".

He must therefore have been aware of the new materials and quotes the results of his own investigations into the comparative efficacy of the materials he has examined thus.

22 tons of (commercial) muriate of potash will produce 100 tons alum

31 tons of black ashes will produce 100 tons alum.

73 tons of kep will produce 100 tons alum.

In these investigations it is the suitability of raw materials which has been under consideration. It is reasonable to ask to what extent the chemistry of the various steps of the process was understood.

Ure and Knapp contributed something to this understanding in their analysis of the clarification process etc. However the first systematic study of the process was carried out by Wilson, a grandson of one of the early partners at the Hurlet plant.

This account, which appeared in the "Philosophical Magazine" of June 1855 followed the process with a series of chemical analyses of the intermediates materials. A comparison of the - ³³⁸not entirely identical - analyses of the shales - raw, calcined and exhausted - provide some points of interest. The results have been collated in the following table:

	Raw Shale	Calcined Shale (Average)			Exhausted Shale		
		Soluble	Insoluble	Total	Soluble	Insoluble	Total
Silica	14.28		36.79	36.79		40.39	40.39
Alumina	26.96	2.08	14.34	16.42		17.25	17.25
Peroxide of Iron		1.68	21.53	23.21		30.66	30.66
Peroxide of Iron and Aluminium					.92		.92
Protoxide of Iron	3.72						
Lime	2.38	1.19	2.91	4.10	1.00	2.22	3.22
Magnesia	trace						
Potash	.24						
Bisulphate of Iron	11.13						
Water	2.02	10.94		10.94	6.36		6.36
Carbon	3.98						
Hydrogen	1.07						
Sulphuric Acid							
Nitrogen	.62	8.87		8.87	1.92		1.92
TOTAL	100.4	24.76	+ 75.57	=100.33	10.20	+ 90.52	= 100.72

The figures in the "Total" column for calcined and exhausted shales are my own additions of the separately quoted figures for "soluble" and "insoluble" materials in these shales. All other figures are as recorded in the article from which it is apparent that the figures are not exactly percentages but close

enough for use in the calculations which follow.

A casual glance at these figures would indicate a very poor level of extraction of aluminium from the shale. But it is worth reassessing these figures in the light of the fact that the mechanism by which the aluminium was rendered soluble was through combination with the sulphur present in the ore.

On this basis a simple calculation shows that at best the sulphur in 11.13g of iron bisulphide (=4g) would combine with no more than 2.25g of aluminium in forming aluminium sulphate. In the analysis this would be quoted as 4.25g alumina. In the two analyses of calcined shale which contribute to the average figures shown in the above table, the highest figure for soluble aluminium is 2.92% with the sulphuric acid almost identical in both samples and hence in the averages (quoted at 8.87%, 8.86% and an average of 8.87%).

Yet as pointed out in the various accounts the loss of sulphur as sulphur dioxide was unavoidable when the alum shale was burned in heaps open to the air and it was for this reason that all such heaps both in Scotland and in North Yorkshire were plastered with wet exhausted shale. It is possible to give some idea of the loss of sulphur using Wilson's figures although this was not attempted in the article itself. 100g of raw shale contained 11.13 iron bisulphide which would give at most 12.26g sulphuric acid after conversion. In fact the calcined shale containing 8.87g sulphuric acid which indicates that expected result of 4.25g aluminium is illusory since the achieved weight of sulphuric acid could "absorb" no more than 3.14g aluminium.

Furthermore the same process which rendered soluble the aluminium also rendered soluble the iron in the raw shale as iron (ii) or iron (iii) sulphate. The solubility of the iron salts is borne out by the results given for peroxide of iron () in the soluble fraction of the calcined shale. Since in the analysis of the raw shale the iron content is analysed as protoxide of iron (FeO) one can only attempt to interpret the conversion to iron sulphate with trepidation.

It is easier to assess the iron by difference; assume that the sulphate ion not in combination with the aluminium has combined with the iron - the only

other metal ion which appears in the soluble fraction, calcium, is quoted as lime and would have been made soluble by conversion to quicklime during calcination and slaking during solution.

Thus the sulphate ion not involved in combination with this aluminium in the 2.08g alumina in the average sample ($8.87 - 5.88 = 2.99$) which amounts to about 34% of the total sulphate ion must be combined with the iron in the form of an iron sulphate. The "better" of the two shales making up the average would give better extraction of the aluminium. The aluminium in 2.92g alumina would be "absorbed" by 8.25g sulphuric acid or 93% of the available sulphate.

Such comparisons are intrinsically spurious since the relative ^{combining} amounts of aluminium and iron could not be easily controlled in the calcining.

The value of the above calculations is in showing that the inefficiency of the above process in recovering aluminium from alum shale cannot be laid at the door of bad management but stands out clearly as a function of the natural mechanism for the process itself. It is clear that a process of digesting the shale in sulphuric acid must necessarily give a higher level of initial aluminium extraction by providing sulphate in excess thus making the aluminium content the limiting factor in contrast to the old technique where the pyrites in the alum shale limited its usefulness. Nonetheless it was a considerable time before the "synthesis" supplanted the old process and for many years the two processes existed together in competition with each other.

Wilson's analysis of the "steeps" during leaching does not add to our knowledge except that separate entries for peroxide of iron and protoxide of iron indicates that the liquor contained both iron (ii) sulphate and iron (iii) sulphate and reinforces the supposition made above.

The reducing concentrations of each species with each successive steep indicates the use of water for leaching instead of the countercurrent "flow" of liquors and shale and a further confusing factor is introduced by Wilson's claim that:

"The potash found in these analyses is derived from the mother liquor which is thrown upon the raw shale previous to calcination".

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Knapp in his analysis of the crude liquor at Gliessen claims that it contains 11.1% aluminium sulphate and 9.8% iron (ii) sulphate. One can understand these results if one assumes that Knapp matched up ions to acid radicals quoting any excess separately. This he did quoting free sulphuric acid as one of his final entries.

The liquor from the steeps is then evaporated, in Scotland, by surface evaporation. During this clarification process a brown precipitate containing "50 per cent sulphuric acid, 25 of peroxide of iron and about 3 or 4 of alumina". This seems to correspond to the slam of North Yorkshire. The brown colour indicates an iron (iii) salt and the analysis indicates a mixture of iron (iii) sulphate and a small amount of aluminium sulphate as predicted in the account of bye products above.

After the "muriate of potash, or sulphate of ammonia, is added, either in solution or dry", and the liquor left to crystallise, the first crystals are observed to be of a brown colour and, on analysis, found to contain 4.52% "peroxide of iron".

The Hurlet process, as mentioned above, involves a double recrystallisation. After the first recrystallisation the peroxide of iron had dropped to 0.88% and on final roaching this species was only identifiable in trace amounts.

These analyses of Wilson show the rationale behind the various steps of the traditional process and a valuable comparison between this and the new "Spence" process could have been given since, as Wilson claims, this latter process, or a very similar one, was in use at Hurlet from 1836.

In this "Spence" process:

"Alum shale containing the smallest amount of sulphur was calcined in a reverberatory furnace; it was then ground and sifted, the powder was thrown into lead cisterns and hot dilute sulphuric acid run upon it. A strong action occurred and the greater part of the shale dissolved. The solution was evaporated and the alkali applied in the usual way; the sulphate of ammonia was at that time made by distilling gas liquor into the mother liquor of the alum; oxide and sulphide were thrown down, and the solution consisted of sulphate of ammonia".

However Wilson does not give a similar analysis for this process and we are left with the above view that, by observation, the extractive process is more efficient with the Spence technique and hence the yield of alum higher.

SULPHURIC ACIDPREFACE

The purpose of this chapter is to sketch the development of the manufacture of sulphuric acid from about the mid eighteenth century to about the mid nineteenth century. This covers the period during which the main developments in technique, plant organisation and control of the "lead chamber process" took place.

INTRODUCTION AND HISTORICAL SURVEY—SUMMARY OF ACCOUNTS OF CAMPBELL AND CLOW ³⁴⁰

Oil of vitriol - the Nordhausen acid - was traditionally produced by the distillation of iron (ii) sulphate. A slow process which produced highly concentrated acid in small batches; it was still a commercial proposition during our period and although not within the scope of this essay it is worth mentioning by way of comparison that six cwts of iron (ii) sulphate produced 64 pounds of vitriol which is less than 25 per cent conversion.

The technique which developed into the large scale process was first used in this country by the notorious Joshua Ward. This process had been in use for many years on the continent and was described in 1670 by le Febres.

It consisted of burning a mixture of nitre and sulphur under a glass "bell" and absorbing the vapours produced in water.

This reduced the price of acid from cost per ounce to cost per pound - a factor of 16.

The mass production of sulphuric acid was not possible in glass jars where increase in size creates increased risk.

The substitution of lead houses as reaction vessels took place in 1746 at the works of Roebuck and Garbutt of Steelhouse Lane, Birmingham. The process used was identical to that of Ward who pursued them for infringement of patent. Nonetheless this plant continued in use for over a century; its final demise being about 1847.

The second Roebuck plant was built in Prestonpans in 1749 and began to export acid to France, Holland, Germany, England and Ireland. It

operated "secretly" for twenty years - Faujas de St Foud found high walls around it - but absconding or sacked workmen carried the process details with them, for example Samuel Falconbridge who went to Bridgnorth in 1756. ³⁴² Other plants were being built at Govan and Edinburgh, at Bradford in 1750, and in Battersea.

Roebuck was unsuccessful in contesting one of these operators (Sterling) for infringement of patent and subsequently the fortunes of Prestonpans declined yet Faujas de St Fond reckoned that in 1784 it was still the largest works in Great Britain.

Following the litigation many more plants were now built; Farmer at Kennington in 1778; Baker Walker and Singleton in 1783 at Pittsworth Moor near Eccles; by 1820 twenty-three plants were using the process to make acid as follows: London (7), Birmingham (4), Bristol (2), Manchester (2), Bolton (2), Newcastle (1). In the Birmingham area there were eight plants .

The process had spread to America in 1793 and was introduced to France by John Holker. ³⁴³

The main advance came when the consumers began to manufacture acid themselves - possibly due to transport difficulties and increase in demand. This latter factor was according to Park ³⁴⁴ due to the needs of the Leblanc process, to a lesser degree "superphosphates" and, until the introduction of saponification under pressure, the manufacture of Stearic acid (also used in soap making). ³⁴⁵

In terms of chronology the bulk user/manufacturers first appeared in the new chlorine bleaching industry. The St Rollox plant was also set up in 1799 to manufacture Tennants' bleaching powder. Initially they bought Prestonpans acid at £60 per ton delivered but by 1803 Tennant had built his own plant burning 1,000 pounds sulphur per week.

In 1811 Thomas Hill and Uriah Haddock patented a process to replace

sulphur with pyrites.

Gay Lussac showed that nitric oxide could be absorbed in sulphuric acid and in 1827 built a tower at St Gobain in an attempt to use this principle to save nitre. The problem created was - what use was the nitrous vitriol produced? This process was rarely used in England until the nitre shortage in the second half of the nineteenth century. ³⁴⁶

The Tennant Muspratt machinations led to a French monopoly on sulphur from Sicily in 1838 which was broken in 1842. In England sulphur never regained its old importance as a raw material and although in France there was no immediate incentive to replace sulphur by 1867 pyrites became the usual raw material in France also. ³⁴⁷

However, price was always the governing factor and as in 1854 a fire revealed a large store of sulphur at ¹Alhusen's works in Gateshead. ₂

Farmer of Kennington tried to replace sulphur by pyrites in 1838 and in 1840 John Allen of Heworth imported the first pyrites into the Tyne and for the next fifteen years the Tyne Alkali men tried to develop burners suitable for roasting pyrites. ³⁴⁸

1866 saw Tennant in the spirit of the 1830s, trying to persuade fellow manufacturers to obtain control of Spanish pyrites and to this end they formed the Tharsis Sulphur and Copper Company which built plants at Glasgow, Tyneside and Widnes.

The company sold pyrites on the understanding that burnt ores would be returned to Tharsis for copper extraction.

Glover in 1859 built first "Glover tower" at the Washington factory of Pattinsons Felling Chemical Company. This was used in conjunction with Gay Lussac's tower. A second tower was erected at Washington in 1861, Wallsend the same year, and in 1864. All the large works on Tyneside adopted the process between 1868 and 1870. It was introduced to Lancashire in 1868; London 1870. Lunge published the method in Dinglers Polytechnic Journal of 1871 which assisted the transmission of the idea to Germany.

Campbell sums up development at this stage thus.

"By the 1870s chamber process reached height of efficiency. Residue from pyrites burners was sold to iron and copper smelters. Spent oxide from gasworks a secondary source of sulphur, nitrous fumes recycled, control of gases ensured continuous production."

At about this period the process which has now superceded the lead chamber process was emerging. Following Phillips patent of 1831 Messler and Squires in 1876 succeeded in combining sulphur dioxide and oxygen over platinised pumice. In their Silvertown works they decomposed chamber acid, passed the hot vapours over a platinum catalyst and absorbed the fuming acid gas in large Woulff bottles. Winkler, a German contemporary, used the same process with platinised asbestos. In both cases the reactants were in stoichiometric proportions and it was only in 1895 that B.A.S.F. "Research and Development Dept" proved that excess of oxygen (for discussion of development of theory see note 348) assisted the reaction. This discovery had little effect in Britain where the demand for fuming acid had decreased. In Germany however, the dyestuffs industry, a large scale consumer of fuming acid, was developing subsequent to the synthesis of indigo by B.A.S.F. In 1905 Lunge suggested anhydrite as a source of the sulphur dioxide.

The scene changed in Britain in the First World War when demand for explosives led the Government to erect plants in Scotland, Lancashire and Yorkshire. Germany, faced with similar problems, used an anhydrite based process.

At Billingham the anhydrite mine was sunk in 1929 and production of acid commenced in 1930 followed by Widnes (1954) and Whitehaven (1954).

I.C.I. gave details of their process to the U.S.A. in 1951 following a gloomy forecast of sulphur reserves in Louisiana in 1950.

During this century the lead chamber process has been progressively replaced by the contact process and in 1971 lead chamber plants are only 25 per cent of total and their production is only ten per cent of the total.

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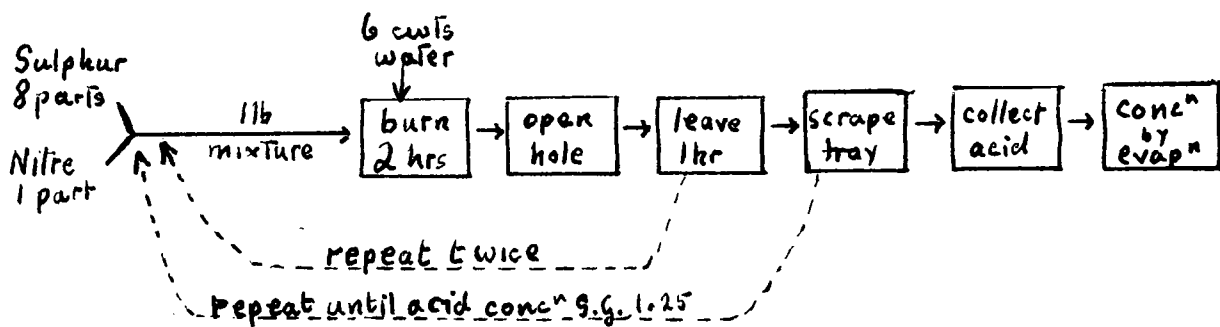
DEVELOPMENT OF THE PLANT TECHNIQUE

Wards reaction vessels or "bells" had a capacity of 40-50³⁵⁰ gallons and although the factory contained many such bells each one was in effect a separate 'plant' since it needed separate tending.

By comparison Roebuck's Prestonpans plant of 1749 consisted of a room containing 30 lead houses each 8½ feet x 6 feet x 4 feet - a volume of 204 cubic feet or 1270 gallons. These chambers were strengthened with wood frames and bedded in sand but ³⁵¹ again each chamber was effectively a separate plant.

The mode of operation was simple ³⁵² - one pound of an 8:1 mixture of sulphur; nitre in a lead tray was put into the 'house' through a ten inch hole near the bottom of one wall. The house contained about ⁵ cwts of water. The charge was ignited and, the hole closed with a lead stopper and the mixture left to burn for two hours. The hole was then opened for one hour, a fresh charge placed on top of the original one and the process repeated. After three charges had burned, the tray was scraped clean of residue (salts). This cycle was repeated until the acid had become concentrated (S.G.1.25) enough for evaporation to be attempted.

This could be represented thus:



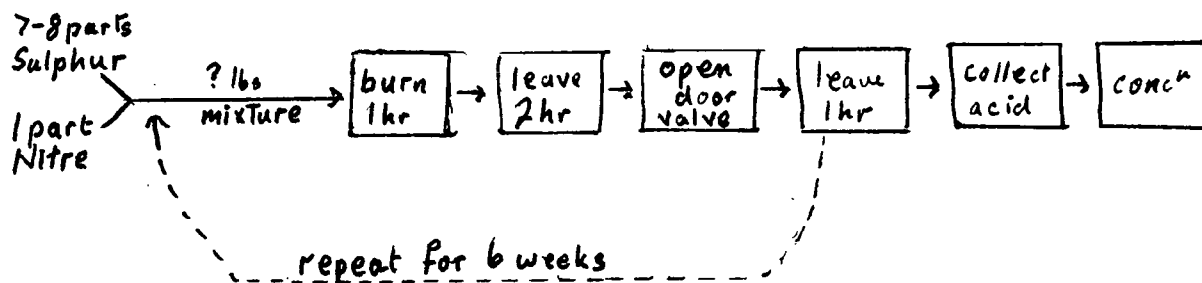
Twenty years later the process was in common use as explained above. Kingscote and Walker at Battersea were using 72 cylindrical cylinders six feet high by six feet diameter - capacity of 70 cubic feet each - plus four cubical vessels of 12 feet edge - capacity 1728 cubic feet - which latter Parkes claims were unproductive and sold as scrap.

These cylinders were formed round wooden cylinders, the ends lapped and soldered and the bottom and cap soldered on. There was only one aperture closed by a mahogany door. ³⁵³

A later plant of 1783 - Baker, Walker and Singleton at Pitsworth Moor near Eccles (Walker was Parkes' nephew) comprised four chambers ^{of} twelve feet edge and four chambers forty five feet by ten feet by twelve feet - capacity 5,400 cubic feet. ³⁵⁴

1799 saw a Manchester plant comprising six chambers ten feet by ten feet by twelve feet - capacity 1,200 cubic feet - each with a door and, on top, a valve for ventilation between burnings. The floors were constructed to hold water to a depth of eight to nine inches - about thirty nine hundredweights of water - and were loaded with 116 charges of a nitre sulphur mixture of 1;7 or 8 introduced on two trays. Combustion took one hour, two hours were allowed for condensation then the door and valve were opened to "sweeten" the chambers. These operations were repeated every four hours day and night for six weeks after which the acid was concentrated in lead vessels. ³⁵⁵

A conjectural representation would be:



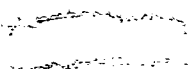
The St Rollox plant set up also in 1799 was a three storey building fifty feet by twenty four feet. On the top floor were chambers; first floor houses concentrating retorts and the ground floor was for initial concentration. The six chambers had dimensions twelve feet by ten feet by ten feet and cost £50 each.

All the above processes involved burning sulphur inside the chambers which produced a residue of "salts" or "sulphur ashes". In 1808 Tennant fitted one of his chambers with an outside furnace and only the vapours were allowed into the chambers. This innovation spread to all the chambers by 1811 on the basis of one furnace to two chambers. The gas flow direction being controlled by dampers. The immediate practical value of this is that it allowed recharging without entering or evacuating the gas filled chambers. ³⁵⁶

The use of steam injection was introduced by De Lee Follie of Rouen in 1774 and to St Rollox in 1813 and 1814. The purpose of this was to keep chambers warm and at that time the real development - of introducing the remaining component (water) in gaseous form - went unnoticed. ³⁵⁷

By 1825 Roebuck's batch process had settled into a practice which could be described thus - note the absence of Tennant's improvement.

The charge - one pound charge to each three hundred cubic feet of chamber - is ignited by burning coals and the chamber luted. Steam is passed in; the amount determined by trial and error. As the reaction gets under way "rain" can be heard on the inside of the chamber and the charge is raked from time to time. (During this time the chamber becomes completely filled with gas). The pressure in the chamber could be controlled by valves or more usually by opening a hole in the charging door whenever creaks, pushes on the walls or the escape of white fumes showed it to be necessary.

The burning lasted twelve hours and a subsequent two-three hours was allowed for condensation of the gases.  The chamber was then hit with a hammer - if this produced an empty ring condensation was complete.

The chamber was then ventilated by opening doors in the sides and roof upon which fumes of nitrogen (iv) oxide emerged. If the emergent fumes had a suffocating smell (due to sulphur (iv) oxide) the operation was deemed bad, otherwise a good operation was acclaimed and the acid obtained was about 50° Beaume (63% acid). 358

The methods described above which were in essence developments of the original Roebuck process are similar in that the chambers were closed throughout the operation and had to be "sweetened" by ventilation before the next batch. This last technique was designated by Smith the "Improved Batch" process who describes an alternate process which was coming into use at the same time. This "continuous" process left the chamber open during combustion so a current of air passed through. (It was some time before steam injection was used in this method). The effluent gas was mainly nitrogen with small amounts of sulphurous and sulphuric acids and oxides of nitrogen which was passed through water to collect the "lost acid" which was added to acid in chambers.

When the charge ceased to burn another charge was introduced immediately and successive charges were introduced until the floor acid was 35°-40° Beaume (42-9% acid).

A tabular comparison of the two processes was given by Smith.

<u>Improved Batch Process</u>	<u>Continuous Process</u>
1. Higher strength 50°-55°B (63-70% acid)	usually 35°-45°B (42°-55° acid)
2. Strong enough for some direct uses (easy to concentrate)	needed to be concentrated by boiling.
3. Chamber had to be left during various operations (above)	quicker more acid/time concentration of purified acid
4. High pressures produced needed control	Pressure did not need control which gave chambers a longer life.

By the 1830s the batch process had given way to the continuous process. 359

The improved methods gave a yield of 250 kg acid from 100 kg sulphur (82% theoretical) compared with the former yield of 100 kg acid from 100 kg sulphur (33% theoretical).

The development of suitable furnaces for pyrites led to this becoming the standard raw material in the 1860s but ^{it} did not supercede sulphur entirely since sulphur produced a purer acid. The pyrites was more available but produced greater wear and tear to the chambers, required more nitre and the pyrite kilns were more expensive. ³⁶⁰

The acid produced was acceptable for processes where the presence of "arsenious acid" ("was constituent of all pyrites") was not an insurmountable evil. The arsenic also corroded the platinum stills ³⁶¹

In practice acid for galvanising, bleaching, dyeing, printing etc needed sulphur as the raw material. Lock and Lock quote analysis by H.A. Smith to show that claims of arsenic free pyrites are not to be depended upon. ³⁶¹

<u>Source of Pyrites</u>	<u>Merchant figure %</u>	<u>Assay</u>
Spanish	0.21 - 0.31	Tharsis 1.651 Mason 1.745
Belgian	trace	0.943
Westphalian	trace	1.878
Norwegian	none	Hard 1.649 Soft 1.708
Irish	0.33	-
Cornish	0.32	-
Italian	trace	-
Swedish	trace	-
Cleveland	-	-

Various methods were used to purify the produced acid of arsenic.

To remove arsenic hydrogen sulphide was added to the acid which was filtered through coke (expensive) or ground iron (ii) sulphide added to acid then filtered. This would make the acid fit for galvanising but not bleaching etc.

"The substance next tried was sodium sulphide added to a known quantity of sulphuric acid in excess of the previously determined arsenic trioxide."

This was followed by coke filtration. This method gave satisfactory results, the expense was moderate but left the problem of getting rid of the H₂S from excess sulphide.

Lock and Lock go on to remark that:

"Another plan tried was addition of common salt to the retorts during concentration but this had no practical results and we trust Mr Smith will not repeat that experiment." 362

An interesting laboratory method which was not used in plants was the addition of the "necessary" amount of sodium hyposulphite to chamber acid (106°Tw) heated to 70°-80°. The arsenic floats on the surface as flakes of arsenic (iii) sulphide (As_2S_3). This was modified to use Barium Chloride which prevents the adulteration of the acid by sodium sulphate. 363

Conscious attempts to avoid complications by selection of pyrites are also outlined.

It is recommended that pyrites containing quantities of earthy carbonate detected by action of dilute acid giving carbon dioxide be rejected since the carbon dioxide would be produced during calcining and interfere with the process.

The cohesive properties of the ore (crumbly versus compact) affected the preparation for the furnaces since the usual process was to break the pyrites into pieces not larger than one and a half cubic inches (does he mean inches cubed?) using a steam stonebreaker or boys using sledgehammers. The latter gives less dust which would otherwise choke the draught in the kilns, Also a poor ore would burn in a bulky mass but a rich ore burned in this way would fuse into slag.

The sulphur content of the pyrites could be determined in three ways:

- a) specific gravity
- b) by mixing 1g pyrites with 2g potassium chlorate and 5g sodium carbonate; heating dull red heat for ten minutes; cool and leach the product; titrate remaining sodium carbonate with sulphuric acid; calculate sulphur in sample by difference.
- c) oxidise pyrites with c. HNO_3 or dil. HNO_3 + KClO_3 , use Barium Chloride to precipitate sulphate and estimate.

Similarly with nitre, the usual impurity was sodium chloride and it was recommended that a sample containing a large amount of "foreign matter" be rejected since platinum used in concentrating the acid is affected by sodium chloride.

The theoretical yield according to Lock is 100 parts sulphur gives 306 parts sulphuric acid at 66° Beaume but usual yield is 275 - 300 parts acid.

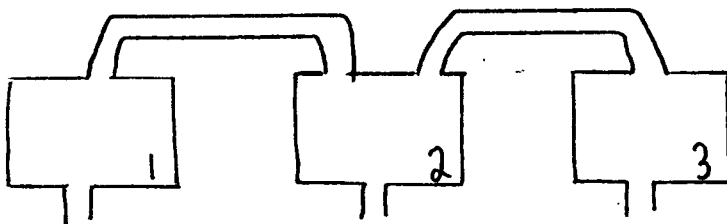
Lock recommends 113 cubic feet air to each 16 pounds sulphur and that the steam pressure should be 40-50 pounds per square inch. Superheated steam was regarded as unsuitable and too much steam reduced the strength of the chamber acid. On the other hand too little steam gave a danger of chamber crystals forming.

Since capacity of kilns determined quantity of material to be burned in a given time the charge must be regularly and unvaryingly supplied.

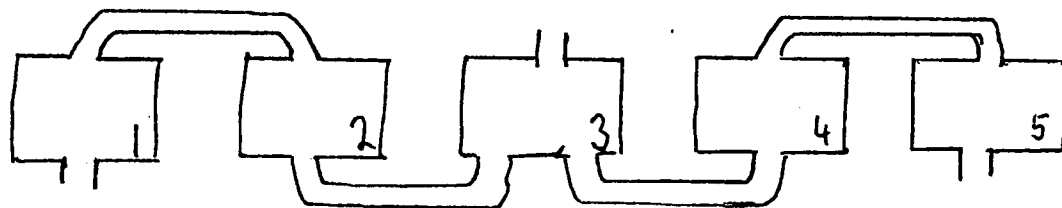
The nitre pots were put in with the charge and contained nitre plus sulphuric acid (three pots in use, two always in kiln). The idea was to facilitate the extraction of all the nitrous gas leaving a soft white cake of sodium sulphate which could be easily removed. If all the nitrous gas not removed then heavy red fumes (nitrogen (iv) oxide ~~fumes~~) are given off when the cake is removed.

Lock advises that the plant manager should keep a chamber Day Book.

The organisation of chambers had developed considerably by 1867. Smith ³⁶⁵ points out that attempts to increase efficiency by dividing chambers or putting them in series had been attempted and Lock gives a number of diagrams where the different chambers in series had stated functions in the process.

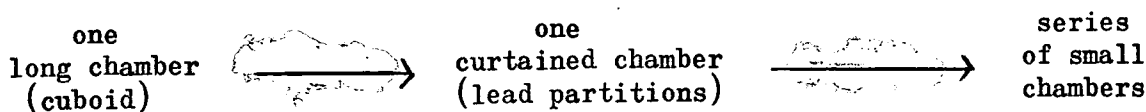


- 1, 2 working chambers in connection with kilns.
3 receiving chamber leading to condenser and chimney.



1, 2 working chambers 3,4 receiving chambers 5 condenser

Lock commented on the need for both large space and area during condensation yet Park ³⁶⁶ claims that even in 1879 when Lunge gave the upper limit of chamber size as 70,000 cubic feet there was no realisation that a large cooling area was needed to "remove heat of reaction." We could summarise the development in chamber design thus. ³⁶⁷



A further advantage of a series of small chambers was that a defective one could be taken off ³⁶⁸ steam and rebuilt without shutting plant.

In 1859 John Glover at the Washington factory of Pattinson's Felling Chemical Company built a tower of firebricks set in molten sulphur and packed with fireclay tiles which was introduced into the flow line between the pyrites furnaces and the chambers. During the year that this tower operated it demonstrated the soundness of the idea of dinitrifying the vitriol by trickling the nitrous vitriol down the tower counter current to the hot burner gas. In simple terms

1. the hot sulphurous gases collected nitric oxide on the way up
2. the dinitrified acid flowed into a reservoir at the base of the tower. 368

The nitrous vitriol was the product of the Gay Lussac tower where waste nitrous gas was absorbed in sulphuric acid flowing counter current to the rising gas. The Glover tower above ^{and} Gay Lussac towers used together solved the problem mentioned i.e. what to do with the Gay Lussac tower's nitrous acid.

The concentration of the acid was accomplished by boiling in open pans³⁶⁹ then, at first, by distilling in glass retorts whose size was naturally limited and the fear of breakage from local overheating led to the use of sand baths or luting the retort ~~body~~ with (say) clay and horse dung.

In 1806 Wollaston made platinum malleable and made the first platinum still in 1809. These stills were often porous and the vitriol oozed through. Soldering with gold was an expensive remedy³⁷⁰ (Smith comments that in France platinum vessels were used in rectification earlier than in Britain and that the Wollaston stills were "inferior to French".)³⁷¹

Sainte Clare Deville melted platinum in oxygen/coal gas blowpipe and this was non-porous. After 1860 these stills were mechanically reliable but not immortal since the arsenic in pyrites ores carried over into the acid and corroded the stills (see above). They were also very costly - that of Lee and Pattinson's at Felling was valued at £924. 15. 0. in 1840.³⁷²

DEVELOPMENT OF COAL GAS MANUFACTURE

EARLY ATTEMPTS

Clow feels there is little to be gained from the early history of gas making before c.1780 since prior to this time

"The Industrial Revolution had not advanced sufficiently to create a demand for longer hours. The emergent palaeotechnic iron industry too would have found it still very difficult to supply (the fittings)." 373

Elton comments that the Napoleonic Wars disturbed imports of Russian tallow and Swedish tar without trying to correlate this to the developments in large scale utilisation of coal gas for lighting in the early years of the nineteenth century. 374

Another factor must surely have been the interplay of personalities involved with the "right man being in the right place at the right time."

The "right man" is in this case William Murdoch, an employee of the firm of Boulton and Watt, known for their entrepreneurial skills. ("The right place") and perhaps the tallow shortage provided "the right time" as far as the mill owners were concerned.

William Murdoch, a native of Bellow Mill, Auchinlick, Ayrshire, joined Boulton and Watt in 1777 and rose to become their principal Manager in Cornwall, which job he held until 1799.

It is now a matter of folk history that in 1792 he lighted his office and house at Redruth in Cornwall with coal gas and lit his way home in the evening using a bladderful of gas as torch fuel.

Was he prompted to attempt these "investigations" by a letter of one John Champion of Bristol to Boulton in 1790 or did he know of the discussions which the junior Watt had had with Dundonald, father and son, about the same time? Both these suggestions were made by Clow. In the event, Murdoch denied having any knowledge of Dundonald's work prior to his own developments of 1805. 375

Elton remarks that Murdoch was being discouraged by the firm at this point. 376

It seems unreasonable, however, to subject Murdoch's early work to this scrutiny. At this point in time, he was merely one of the small band of people

who in the closing decades of the eighteenth century had utilised coal gas on a small scale for such operations. To give some examples, Professor Minckeler³⁷⁷ had lit his lecture room at Louvain University with coal gas in 1784. George Dixon, a small coalowner of Cockfield, Durham, had lit his house similarly (a very primitive arrangement)³⁷⁸. Lebon in France was using gas to light his house and gardens at the same time as Murdoch³⁷⁹.

In 1798, Murdoch, using an iron retort,

"erected an apparatus for the production of gas at the manufactory of Messrs Boulton and Watt at Soho".³⁸⁰

Lebon in Paris was also involved in developing gas lighting and in view of the contacts of the Watts with Paris at this time, one suspects that what was known in Paris was known in Soho. So much so that the promise shown by Lebon's work led Watt junior to write home in 1801 urging that Murdoch commence developing immediately.³⁸¹

Both Lebon and Murdoch used gas lighting displays to celebrate the Peace of Amiens in 1802. In the event, Murdoch's display consisted of two "Bengal flares" attachments at each end of the factory fed from a retort placed in the fireplace.

Clegg junior asserts

"This was the only gas used on that occasion, the rest of the manufactory being illuminated by the usual small glass oil lamps and not with the gas as has been erroneously stated."³⁸²

The "erroneous statement" probably derives from the more ambitious plans which had been devised for this occasion, but not executed.³⁸³ Clegg claims as his source for the above claim, his father who was at that time a 'pupil' of Murdoch's and present on this occasion.

The Soho foundry was illuminated by gas the following year with the retort feeding the burners via a gasholder of depth 6 feet and diameter 8 feet. The retort was as described above.³⁸⁴

This retort suffered from the coal being present in a bulky mass which led to waste of heating fuel. The heating area i.e. the outside of the retort,

was too small compared to the mass of coal and since the coal was being slowly converted to a coke from the outside in, heat transfer became progressively slower as carbonisation progressed.

Murdoch began to experiment with different retorts moving from the squat cauldron to the long cylinder. The first setting of this cylinder gave some improvement in the problems outlined above but made removal of coke more difficult.³⁸⁵

The design which quickly became the accepted one for many years was the horizontal cylinder which made coke removal easy and gave a large heating area compared to the mass of coal. Further experiments on the shape of the cylinder continued with Murdoch and later with other workers (e.g. oval, ear shaped, etc.).³⁸⁶

Nevertheless, when Murdoch in 1805 lighted the cotton mills of Messrs Phillips and Lee at Salford, the retort was similar to the original model - parallel sided without a coke hole in the bottom, the coal put in and coke removed using a crane.³⁸⁷

HENRY'S RESEARCHES

As well as the "chemical engineering" research conducted by Murdoch, extensive related research began at this point in the field of applied chemistry. William Henry made many investigations on gas plant at Phillips and Lee's works.³⁸⁸ Elton³⁸⁹ claims that Henry, in fact, helped Murdoch in his development work. Buckley and McCulloch have discovered and presented manuscript evidence of Henry's researches as the Phillips and Lee gas plant.³⁹⁰

A summary of Henry's work is presented by himself in a paper read to the Royal Society on 22 February 1821 and can be illustrated in this extract.

"In the first of these essays (Nicholson's journal 8 June 1805), I detailed a series of experiments on the gases obtained by the destructive distillation of wood, peat, pit coal, oil, wax, etc from which it appears that the fitness of these gases for artificial illumination was greater as they required for combustion a greater proportional volume of oxygen; and that the gases generated from different inflammable bodies or from the same inflammable substances under different circumstances, are not so many distinct species, which under such a view of the subject would be almost infinite in number, but are mixtures of a few well known gases, chiefly of carburetted hydrogen with variable proportions of olefiant, simple hydrogen, sulphuretted hydrogen, carbonic acid, carbonic oxide and

azotic gases; and that the elastic fluids obtained from coal oil etc have probably in addition to these, an inflammable vapour diffused through them when recent which is not removed by passing them through water. In the same paper, I explained certain anomalies that appeared in the experiments of the late Mr Cruickshank of Woolwich, which are not at all chargeable as errors upon that excellent chemist and could only be elucidated by further investigation of the gases to which they relate - to Mr Dalton also we are indebted for an accurate acquaintance with carburretted hydrogen gas and for much information that is valuable in assisting us to judge of the composition of mixed combustible gases by the phenomenon and results of firing them with oxygen.

"In the second memoir (Philosophical Transactions 1808), I described a series of experiments on the gases obtained from several different varieties of pit coal and from the same kind of coal under different circumstances. Various species of that mineral were found to yield aeriform products, differing greatly in specific gravity combustibility and illuminating power; thecannel coal of Wigan in Lancashire being best adapted to the purpose and the stone coal of South Wales, the least so. In decomposing any one species of coal, the gaseous fluids were ascertained not to be of uniform quality throughout the process, but to vary greatly at different stages; the heavier and more combustible gases coming over first, the lighter and less combustible afterwards. By subsequent experiments on the gases obtained from coal on the large scale of manufacture, it was found that a similar decline in the value of the products takes place but not to the same extent, owing, probably, to the greater uniformity of temperature which is attainable in large operations." ³⁹¹

The analysis giving rise to these conclusions were tabulated in the papers e.g. this table shows gas composition related to progress of carbonisation.

GAS FROM WIGAN CANNEL COAL

TIME OF COLLECTION	SPECIFIC GRAVITY	ABSORBED BY CHLORINE	LIGHT CARBURRETTED HYDROGEN	CARBONIC OXIDE	HYDROGEN	NITROGEN
1st hour	0.650	13	82.5	3.2	0	1.3
	0.620	12	72	1.9	8.8	5.3
	0.630	12	58	12.3	16	1.7
5 - 10 hours after commence	0.500	7	56	11	21.3	4.7
	0.345	6	20	10	60	10

(These results have been confirmed by later workers on many occasions). The fact that a particular coal quality was preferred shows again a conscious determination of process factors.

Cannel coal, the preferred raw material is described by Van Kreuvelen and Schuyer as a dull black coal with a conchoidal fracture. ³⁹² A splinter of this coal can be lighted with a match and its derived its name from the word

"candle" since it burns with a long and steady flame. Its origin is attributed to spore accumulations in the vegetable muck of the carboniferous. (See Accum below for research in coal choice).

The first gas plant was in many ways a pilot plant or was in fact treated as such by Boulton and Watt, Murdoch and Henry. That this should be possible in a working mill, owes much to the management and one of the partners, George A. Lee (1761 - 1826) has been described by Robert Owen as "one of the most scientific men of the day". He was a friend of Thomas Boulton and James Watt, Peter Ewart, William Street, William Murdoch and William Henry to whom he gave assistance in his chemical researches to improve the process. ³⁹³

Further experiments by Henry Creighton ³⁹⁴ show many more of then known factors in the process. The total quantity of light produced by the unit in full operation was assessed as equivalent to 2,000 "mould candles" which consumed tallow at the rate of 4/10 ounces per hour. The illumination was provided by 271 Argand burners - the Boulton and Watt firm had modified the original oil lamp design to allow it to be used with gas - 633 Fleur de lis shaped burners (dubbed 'Cockspurs' by the workmen).

The Argand and Cockspur burners were rated as equivalent to 4 candles and $2\frac{1}{4}$ candles respectively.

The total gas demand was assessed at $1250 \text{ f}^3/\text{hr}$ which could be produced by $3\frac{1}{2}$ cwt of cannel coal (capacity of the retorts was 15 cwts of coal each).

Boulton and Watt had tried to purify gas chemically but at time of installation, gas still gave some noxious odours although it seems likely that the gas holder would contain lime in water. In any case, Clegg notes that ³⁹⁵ siphons ³⁹⁶ were needed along pipes to collect condensing tar.

THE '1805' PAPER TO THE ROYAL SOCIETY

Most of these details of operation together with a costing of the process which claimed its advantages over traditional illumination were presented to the Royal Society on 25 February 1805 in a paper read out by Sir Joseph Banks in the name of William Murdoch. ³⁹⁷

Clow claims that this paper can be found in draft with all corrections and amendments in the Boulton and Watt papers and none of it is in Murdoch's writing. He further claims that while the paper was being prepared, Murdoch was in Portsmouth attending an engine. The paper was therefore prepared by Watt senior and junior and furthermore, the experiments described were carried out at Phillips and Lee by H Creighton.³⁹⁸

The whole operation seems to resemble a well thought out operation since "the man" - Murdoch - despite the needs of "the time" - war shortage - would have achieved nothing without the investment of Boulton and Watt, who had initially laid out £4-£5,000 on the venture and who, by mid 1806, had stocks of 1,300 burners and 10,000 feet of gas tubing. This had increased by a factor of three by 1807 when in addition, they had on order 12 retorts, 100 patent lamps, 5,000 burners and 4,000 feet of gas tubing.³⁹⁹

EARLY COMPETITION

Nor was this the only operating plant for gas illumination in 1805. Clegg, who as a Boulton and Watt employee must have learned much during the development stage, was in competition with Murdoch and they were racing neck and neck to complete the "first installation". Clegg according to his son, won narrowly and the son writing in 1841 describes how:

"In the Cleggs journal which I have before me, it is stated that the cotton mill of Mr Henry Lodge at Sowerby Bridge near Halifax was lighted with gas a fortnight before that of Messrs Phillips and Lee; Mr Clegg had made his men work overtime in order that his apparatus might be the first completed, there being a friendly spirit of emulation between Mr Murdoch and his pupil in advancing the progress of gas lighting."⁴⁰⁰

Murdoch, in a letter to Boulton and Watt, seems to raise this claim above the level of filial loyalty as well as giving a wry insight into the "friendly emulation". It seems more a case of cut-throat competition. He wrote on 12 December 1805:

"If material cannot be forwarded in a more expeditious way than they have hitherto, it is no use to think of taking orders here for your old servant Clegg is manufacturing them in a more speedy manner than it appears can be done at Soho".⁴⁰¹

In spite of the pioneering work of the Boulton, Watt, Murdoch, Henry

consortium, we must now turn to Clegg to observe the further development of gas lighting techniques (Murdoch carried on installations for many years and Henry's contributions to gas lighting research continued also, especially in analysis).

Elton concludes:

"... Murdoch, Boulton and Watt ... did not grasp the significance of the fuel which they did so much to perfect. The development of the gas industry ... is not so much due to them as to such men as Winsor ... and the elder Clegg." ⁴⁰²

The most pressing problem was to find ways of adequately purifying the gas, especially in the removal of ammonia and hydrogen sulphide which were in the main responsible for the "offensive effuvia" and which caused headaches and could affect the lungs ⁴⁰³ (ammonia). ⁴⁰⁴ Hydrogen sulphide is as poisonous as hydrogen cyanide but is happily detectable by its smell in very small concentrations.

Lime was used to absorb both these gases. Who first introduced it? Elton claims that the lime process as such was invented by Henry or Heard. ⁴⁰⁴ Clow feels it was probably used in Phillips and Lee installation by Murdoch, merely by adding lime to water in ^{the} _λ ⁴⁰⁵ gasholders.

Clegg developed its use by adding a paddle to the gasholder which was installed in part of the apparatus in the gas lighting plant at Harris' mill at Coventry 1809. ⁴⁰⁶ It was difficult to remove spent lime from a gasholder in an operating plant without shutting down the operation. It would be interesting to have figures on H_2S versus lime in the life cycle of one such lime change. One suspects that the limits of tolerance would be fully stretched if the alternative was shut down.

The problem was much more acute when Stoneyhurst College was illuminated by gas in 1811, since the gas would be very unsafe in small rooms. A separate purifier was inserted in the gas flow prior to the gasholder. Thus spent lime would be removed and fresh lime added. This particular design was not operated for long. ⁴⁰⁷

Subsequent developments were introduced in the time honoured manner of improving on past work in each successive installation and as the lighting of mills with coal gas proceeded. Mr Greenaway's Manchester works saw the first

hydraulic main used to clear up the condensation problems. At Mr S Ashton's works 1812 we have an improved lime machine, hydraulic main, 12 inch cylindrical retorts with improved mouthpieces and a control on the gasometer to regulate specific gravity. ⁴⁰⁸

In the same year, Clegg installed a gas lighting system at the premises of Rudolph Ackerman, printseller, 101 Strand, consisting of two horizontal retorts holding 240 pounds of coal (half cannel half Newcastle) yielding 9.300 F³/ton and requiring a heating charge equivalent to 21 per cent of coal carbonised (or 42-46 per cent on a cold start). Although this installation soon highlighted the problem of spent time disposal yet again (complaints about stench when lime was dumped in river led to use of cream of lime which was required in greater bulk - ⁴⁰⁹ no one at that point had realised the simple fact that surface area was the important factor) this must have been a useful operation in prestige and publicity for new process. ⁴¹⁰

TOWN GAS LIGHTING SUPPLY : ORIGINS AND DEVELOPMENTS

Since about 1805 Winsor (originally one Friedrich Albrecht Winzler or Winzer from Znaim Moravia) had been trying to provide urban gas lighting. At first he tried to float the "National Heat and Light Company" promising returns of 11,400 per cent. By 1807 a few lamps had been installed for propaganda purposes in Pall Mall and parts of Beech Street and Whitecross Street. In 1809, he and others applied to Parliament to incorporate a Company to be known as "The London and Westminster Chartered Gas-light and Coke Company" but the collective opposition of the public and Murdoch and Watt prevailed. Undismayed they petitioned again the following year and the enabling Act was passed in 1810 with numerous stipulations. ⁴¹¹ The company was incorporated in 1812 under the directorship of Friedrich Accum. Clegg became engineer to the company in 1813 and his son recorded later that his first task was to discard the existing plant and invent the necessary equipment and instruct workmen. ⁴¹²

To overcome initial sales resistance shops and houses were fitted free of charge as an inducement to attract customers. ⁴¹³

The shortage of suitable piping led to the use of musket barrels screwed together.

Prejudice was more difficult to overcome. Davy quipped that in lighting London a gas holder the size of St Paul's dome would be required - a prospect not at all daunting to Clegg, as he remarked in reply. But size and safety of holders continued to worry the public and initially the insurance companies. A Royal Society deputation recommended to the Government that the gas holders should be housed in strong buildings and have a capacity of not more than 600 F³ in spite of (or possibly because of) Clegg attempting to prove the nonsense of these requirements thus:

"As Sir Joseph Banks and some of the other members of the deputation were conversing upon the danger of a leak in the gasometer if a light happened to be near, Mr Clegg called to a man, desiring him to bring a pickaxe and candle; he then struck a hole in the side of the vessel and applied a light to the issuing gas, to the no small alarm of all present, most of whom quickly retreated; contrary to their expectation, no explosion resulted from this experiment." ⁴¹⁴

In 1813, however, an explosion caused when replenishing the lime purifier and injuring Clegg would have done nothing to bolster the shaky public confidence. It led to the use of a water seal on the purifier. Westminster Bridge was illuminated in 1813 and in 1814, the Parish of St Margaret's Westminster followed ⁴¹⁵ (in spite of the pressure of the "oil gas" interest - in any case it is not to be thought the company had a monopoly, they were prevented from having this position by the Act of 1810. To put the matter in perspective, they operated in two areas, Norton Folgate to west end of Cheapside and Pall Mall and Westminster to Temple Bar. In between rival companies were operating and other companies were being formed to supply Southwark and the East End. ⁴¹⁶

In June 1814, the St James Park Pagoda - a gas lighting spectacular for the allied sovereigns - was burned to the ground due to Sir William Congreves fireworks display, according to Clegg junior. The gas was blamed nonetheless. ⁴¹⁷

In 1815 the Guildhall was illuminated by gas - also good for prestige. ⁴¹⁸
There were no gas chandeliers as such. Dixon was prepared to make them and

Clegg had modified the usual design by using a hollow chain. At about this time a Batswing burner was invented by one Stone, a workman of Winsor (although according to Clow, this was devised by Neilson of the Glasgow Company Limited). However, it is not reasonable to ascribe to one man the invention of such a simple device.

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Clegg had devised a gas meter in 1815 which was improved by Malam, his son-in-law in 1819. Clegg's other improvement included a gas governor to give constant pressure and a mechanical retort which was used later in Chester, Birmingham, Bristol and the Royal Mint. Winsor and an employee also claimed to have introduced a lime process where the lime was put into the retort with the coal. In 1817, came Reuben Phillips' patent for dry lime purification of the gas. This remained the usual method until Richard Laming's French patent of 22 February 1849 advocating use of Iron Oxide (revivifying oxide) to remove hydrogen sulphide.

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The spent oxide could be revived by roasting and used again (this could be profitably combined with production of sulphuric acid).

The extent of gas making in London brought out by Accum who claimed that in 1815, London had 26 miles of gas main supplying 4,000 Argand burners but by 1819 there were 288 miles of gas main supplying 51,000 burners.

423

By 1819 two textbooks had appeared on gas manufacture of which Elton says:

424

"Accum's is a scientific treatise outlining the chemistry of the coal gas process describing gas manufacturing appliances in detail and discussing experimental methods of determining the best shape of retorts and optimising carbonising periods and temperatures. Peckston is more interested in how best to maintain and run a gasworks".

MEASUREMENT OF ILLUMINATING POWER

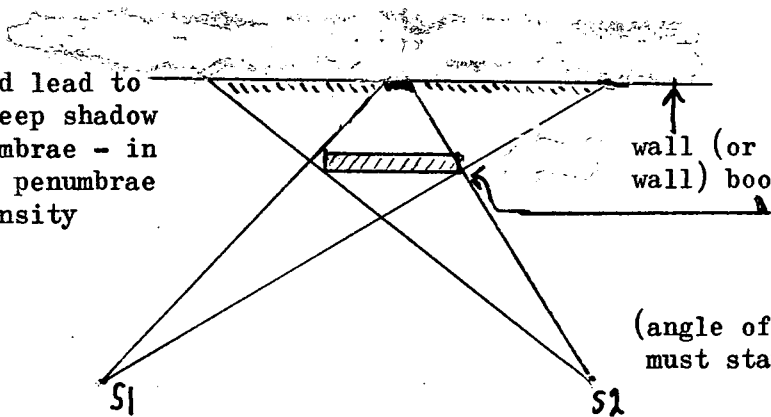
Accum, for example, described clearly the way in which illuminating power of burners could be measured thus:

425

"Though the eye is not fitted to judge of the proportional force of different lights, it can distinguish in many cases with extreme precision, when two similar surfaces presented to the eye together are equally illuminated. But as the lucid particles are darted in straight lines, they must spread uniformly, and hence their density will diminish in the duplicate ratio of their distance. From the respective situation therefore, of the centres of divergency, when the contrasted surfaces become equally bright we may easily compare their relative degrees of intensity".

This could be shown diagrammatically based on the equipment described on page 24 of the same volume.

position could lead to a region of deep shadow with two penumbrae - in this case the penumbrae of equal intensity



S1 and S2 move along lines 1 and 2 until uniform shadow achieved.

In describing the gas works at Ackerman's house and the early town gas works he shows clearly the developments made by Clegg.

The iron retorts are heated in a retort furnace made of firebricks.

The tar is trapped in a tar cistern which later acts as a tar seal by letting the delivery pipe dip into the tar.

GAS LEAK AND PRESSURE CONTROL

The gasometer is identified as "collecting and preserving", "distribution and applying" the gas but on page 85 "equalise" ^{to pressure}. It is counterpoised to prevent rapid movement and rapid pressure change; on page 181 there is a discussion of pressure control (S.G.) of gas by calculation of counterpoise.

Accum includes Clegg's notes for operatives which show ^{an} aspect of control - workmen were instructed to check for leaks in gasometers at least once a week with ^a candle or if this fails lead paint, which will turn brown over ^a leak; if only a smell, mend leak with beeswax. ^{u27}

CLASSIFICATION AND SELECTION OF COAL ^{u28}

By this time the second volume was published in 1819. Accum includes analysis to determine ^{the} gas making characteristics of various coal ^s which he divides into three classes on the basis of his analysis.

First class are chiefly bitumen giving no swelling or caking and leave light ashes between 10,000 and 20,000 f³ per chaldron of gas.

The Newcastle coals give 15-16,000f³/chaldron compared to the cannell coals

Scotch cannel as standard Newcastle and Forest of Dean were similar 1.04, 1.08, but Hutton Seam, Tyne Main and Warwickshire coal took much longer to carbonise.

He realised the inadequacy of bulk heating and clearly stated that coal should be carbonised in thin layers about two inches - four inches thick (see also below).

Accum also compared the efficacy of different retorts and retort arrangements by performing the experiment on progress of carbonisation above with 36 parallelopipeded retorts each containing two bushels of coal and using Peckston's results for 18 cylindrical retorts containing each one chaldron of coal.

He commented that:

"The same heat which is necessary during the first hour of the operation for the evolution of one hundred and fifteen cubic feet of gas is required in the eighth hour for the production of no more than forty two cubic feet, being a decrease of two thirds.

"When large retorts are employed for decomposing coal in masses, from five to ten inches in thickness, the loss of heat is in a much greater ratio".

Previously he had explained the reason for this:

"It must be obvious that in proportion as the mass of coal in the retort becomes carbonised or converted into coke the exterior surface becomes a gradually increasing obstacle to the action of the heat upon the interior or central part of the coal remaining to be decomposed. The heat required on that must be more intense and kept up to no purpose and the extraction of gas becomes slower and slower as the operation proceeds."

In spite of this, he quotes a cost benefit analysis by Peckston of two modes of operation, 1) leaving the retorts for eight hours or 2) terminatint carbonisation after six hours, and gives an italicised conclusion.

"Let the number of retorts worked be what it may, an advantage will always be gained in the mode of manufacturing coal gas, by working the retorts at eight hour charges as the workmen call it, in preference to adopting the shorter process."

INDUSTRIAL "TAKE OFF"

The explosion in town gas provision was immense in the second and third decades of the nineteenth century! In England, the following towns had been equipped by 1819; Bristol, Birmingham, Chester, Kidderminster, Worcester (all inaugurated by Clegg) Liverpool, Bath, Cheltenham, Leeds, Exeter, Macclesfield, Newcastle-upon-Tyne. In Manchester, the Police Commissioners gave a contract

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to the engineering firm of Peel and Williams to build the "public gas works" 17 August 1817. This caused something of a scandal as Williams was a member of the gas committee. The Manchester gasworks are also interesting in that John Dalton was involved in consultancy there. ^{u32}

On 11 November 1824 the Management stipulated that "Mr Dalton have access to gas works at all times" and the following year he was to give expert evidence again before ^aParliamentary Committee on the gas bills.

In Scotland where they have more cannel coal than in England, gas lighting ventures had kept pace with England. By 1805, Andrew Ure was lighting his lecture theatre at the Andersonian with gas and ⁱⁿthe Town, Lumsden's (booksellers) J & R Hart (baker) and Aulton Spinning Works were similarly lit. Shortly after the English mill illuminations, Scotland followed suit and in 1817 the Glasgow Gas Company was formed (street lighting commenced on 5 September 1818). The Edinburgh Gas Company started at the same time under Sir Walter Scott as Chairman (probably on oil gas). The subsequent history is less telescoped than in England. Aberdeen 1824 (oil gas from fish oil), Dundee 1825, Greenock 1827, Banff 1830, Hamilton 1831, Peterhead 1833 and Turriff 1838. ^{u33}

In North Americas Baltimore was supplied in 1819 followed by Boston 1822 and New York 1825. ^{u34}

The eternal projector F.A. Winsor had started gas lighting in Paris in 1815 using oil gas plant by Phillip Taylor. ^{u35}

Elsewhere the "Continental Gas Association" of Sir William Congreve supplied Berlin and Hanover (1826) Aachen (1838) Cologne (1841) and Concurrrenz Anstalt (1845). Dresden was supplied by G.M.S. Blockmann in 1828. ^{u36}

None of these companies were in any sense public utilities which Elton ^{u37} seems to think was Winsor's original idea (this does not seem to square with his wild promises quoted above). They were profit making companies in continuing conflict with the public. Clow ^{u38} analyses the 1818 conflict in Newcastle upon Tyne where net return on capital sunk was 57 per cent in one year i.e. pure profit in less than two years.

Developments continued. In Scotland the Glasgow Gas Company had

appointed James Beaumont Neilson as foreman and later as manager and engineer. He studied at the Andersonian to improve his chemistry and physics. He is noted for using iron sulphate solution in addition to lime for purifying the gas (this reagent is mentioned by Accum in addition to "sugar of lead" which was and is the standard test for hydrogen sulphide and the lead acetate paper was an early development). He used hot charcoal to absorb tar and oil but especially is noted for introducing fireclay retorts - iron retort^s had short lives and in any case led to low temperature carbonisation. The use of refractory ware increased the life of retorts and allowed higher temperature. ⁴³⁹

BY-PRODUCTS

The disposal of by products is not strictly a process control matter but must be considered for a full picture. Complaints arising out of disposal of discard^s are mentioned above with respect to lime. Tar and ammonia liquor were originally discarded also to cause a public nuisance. From 1819, however, Mackintosh used the Glasgow waste. He could utilise ammonia directly and also the pitch derived from tar, but he was left with a naphtha residue. This became a profitable line when he found it would dissolve caoutchouc and that a garment impregnated with the solution became waterproof. His further development of a tar burning furnace helped recycle tar and became a universal fuel economy on gas works until tar became a valuable raw material later in the nineteenth century.

The chemical development of by products which were such a feature of the later nineteenth century and early twentieth century had to wait for the analyses of coal tar which took place piecemeal during the next century (even now the book "Known constituents of coal tar" is a loose leaf binder). Miall briefly gave a chronology assuming 1812 as ^{the} start of ^{the} gas industry.

- 1819 Alexander Garden discovered naphthalene in distillation products.
- 1825 Faraday discovered benzene in whale oil.
- 1826 Unverdorben^a discovered aniline in distillation of indigo; shortly afterwards it was found that it could be prepared from nitrobenzene.
- 1832 Dumas, Laurent discovered anthracene in coal tar residue.

1842 Leigh (?) discovered benzene in coal tar. ⁴⁴⁰

CONCLUSIONS

It would be extraordinarily presumptuous to make any claim that the questions raised in an enquiry such as this are capable of a neat answer. All questions raised and apparently answered beget a brood of questions which require further research and for which it is not yet certain that the material, whether in manuscript or otherwise, is now extant. For this reason I will separate the conclusion into two parts and first will present the thesis or hypothesis which I believe the facts will support, and in the second part outline what I consider the main "loose ends" which I consider worth further consideration. In this second part it is certain that any reader will have observed before reaching this point many unanswered questions which may have exercised his mind but which I have not considered explicitly. This I feel is ~~unavoidable~~ unavoidable especially when one uses manuscript evidence.

REVIEW OF WHAT MAY BE DEDUCED FROM THE EVIDENCE PRESENTED

Many of these conclusions have already been presented explicitly or implidly in the sections concerned but it is worth collecting them together to obtain a fuller view. It is also worth separating the industries.

1. ALUM

It seems obvious that control tests using density and simple analyses resembling primitive filtrations were in use early in the eighteenth century and the control tests were systematic in the latter half of that century. Furthermore improvements were made that were recognised to the extent of rewards being given as in Dodd's improvement in extracting lees from Kelp. The raw materials changed following relevant research being published (vide Vanquelin p 112). After the turn of the century a laboratory was established as borne out by the first Laboratory notebook of 1805 and successive laboratory investigations. Reference to a specified laboratory and its contents appears in the inventories from 1827 . A chemical consultant's (Faraday) advice was sought and his recommendations followed up in the laboratory. Perhaps more important to this view of a scientifically concerned management is that from 1820 - as recorded in the inventories - a library was maintained in the alum house, presumably, for

the use of plant management - the owners would have a library in their palatial residence for their own use. The individual books were listed in the inventories and, with few additions of note, was donated to a local improvement society in 1867 on the demise of the plant. ⁴⁴¹ This list of books reproduced as pages ¹⁴⁹ seems to me to be without doubt a working library for a scientifically oriented management. Throughout the period considered I believe the evidence demonstrates sound organisation, delegation and financial and scientific control of the North Yorkshire industry by a group of professional managers who, although obviously in command of plants belonging to different owners, were brought together by mutual interest and the operation of the cartel.

However I have found no evidence of a formal grouping until the publication of Watson's book at the behest of the society of "Alum Makers".

2. SULPHURIC ACID

In this industry although of later origin than alum, the use of density was early introduced as ^a test for completion of the combustion of the mixture in the chambers. The true importance of the "steam injector" - it is argued - went unnoticed and doubt has been cast on the effective influence on manufacturers of the paper of Clément and Desormes. However it is in this industry that we find practitioners referring to themselves, at an early date, as chemical engineers and even the early plant owners/managers were recognisably men of chemical education - Roebuck, Chaptal, etc. My account is essentially based on published accounts and I believe that - if available - manuscript sources would show as well run and scientifically organised an industry as alum.

3. ILLUMINATING GAS FROM COAL

Here we have an industry which like Mendeleev's Table was born ["]fully grown.["] After the first decade of private contracts the town gas projects demonstrated extensive chemical engineering skills in transport of materials involving initial purification gas pressure and hence flow control. The scientific selection of raw materials and design of carbonising vessels to establish uniform heating of thin layers together with tests to establish the illuminating quality of the product emerged with the first published textbooks on the process. The

- 2 Vols: Atkins Chemical Dictionary 149
 5 " Thompson's Chemistry
 2 " Henry's — " "
 2 " Accum's — " "
 2 " Fourcroy's — " "
 2 " Chaptal's — " "
 2 " Lavoisier's — " "
 4 " Murray's — " "
 2 " Newmans — " "
 2 " Edinburgh Gazetteer
 3 " Parkes Chemical Catechism
 5 " — " Essays
 1 " Accum's Tests
 1 " Edinburgh Dispensatory
 4 " Beekman's Inventions.
 1 " Scotch weights & Measures
 1 " Hamilton's Merchendize
 1 " Land Measurers Tables.
 1 " Thompson's Market & "
 1 " Curwen on Draining
 1 " — " — " — Feeding
 1 " Yorkshire Poll Book
 4 " Burns's Justice.
 Nos Barnes' French Revolution
 1 " Parkes Chemical Catechism
 1 " Brande's Chemistry.
 1 " Brown's Husbandry
 1 " Schener on Blowpipe
 5 " Encyclopedea Britannica.

The above volumes were handed
 into the Library of the Loftus Mental Improvement
 Society in 1867 by A. McKeown.

Edwin V. Dixon

Secretary

developments in purification and utilisation of bye products followed on analyses of the oils and tars produced which took place piecemeal after the first developments. Efficient illumination came extremely late with the invention of von Welsbach's mantle but this need not blind us to the early chemical engineering developments; scientific research of Henry; technical research of Accum; consultancy of Henry and Dalton and the use of simple tests for the gas.

PROFESSIONALISM

This, to me, is the main question left open in the introduction which I feel is still open.

It seems clear to me that the basic functions of works chemist and chemical engineer were being carried out in the industries considered. However in the first case there is no "profession" of works chemist and in the second case, although one or two gentlemen described themselves as chemical engineers in the 1870s, there seems to be no evidence that a group of people were linked together by such a common title.

Certainly Dr Russel's criteria for what constitutes a profession namely "Intellectual Qualifications", "Social Responsibility", "Remuneration", "Community Relationships" and "Authority" are not in any way met in the historical time intervals covered by the above studies.

However it seems reasonable to ask whether a profession of the self regulating, ^cexclusive variety - setting its own charges; controlling its own entry; and existing as the authority to which the public or other bodies would look for expert advice - is the sort of model applicable to the field of industrial functions.

Many bodies - such as the Coke Oven Managers' Association - exist, having been formed by practitioners, to further the aims of better understanding and better communications of developments etc. Such organisations are represented on British Standards sub-committees and contribute to the foundation and monitoring of examinations courses which contribute to better training. Contrary to this the post of "Works Chemist" when advertised does not normally require specific education other than in chemistry, but may require specific experience. But it may be argued that works chemists are a sub group of the chemical profession whose professional voice is the Royal Institute of Chemistry, and many, although not all, would seek such recognition which they may find more possible under the newer regulations.

The managerial group in the alum works in North Yorkshire showed strong

"Community Relationships" and had a strong feeling of collective identity; they delegated duties to clerks and alum makers and the alum makers went on to form a Society for which Watson wrote his 1854 paper but neither the original group of managers nor the latter group of alum makers can lay claim to professional status in the sense outlined in Dr Russel's text.

The sense in which profession could be used in our case is possibly as a synonym for a status or recognisable position. The Yorkshire Directories list "managers" of the alum works and occasionally "alum makers". A man would describe himself as "works chemist", "plant manager" etc with some expectation that his hearers would appreciate his status and possibly understand his duties.

After this brief summary of the two ways in which I think the origins of "professions" can be viewed, I must end by arguing, tentatively that it is of more value to the modern "professional" manager, works chemist, etc. to be able to identify his own function stretching further back into the chemical industry than to seek to give a separate accolade of "profession" or see them as part of the development of a general chemical profession, in which development the chemical consultants mentioned in the account seem more obvious progenitors.

Tentative indeed must any such conclusion be since little is known of the managers except their names and the details of their jobs. Their backgrounds, education and indeed date of death are as yet undiscovered. Of the "works chemist" we see only the function. It is not certain that only one person was involved in this function and if anyone else other than the agents were involved we cannot be certain that we even know their names. A deeper and more extensive examination of manuscripts and the search for new sources would possibly lead to a greater understanding of these "professional classes" of the eighteenth and early nineteenth century and the local net must be spread wider to include George and Jeremiah Dixon, John Bird, and possibly Thomas Wright, all of whom lived in South Durham and North Yorkshire area in the second decade of the eighteenth century. All of these were neither workmen nor important figures in society; they were educated but not members of any recognised profession at that time and their education did not include university studies. To me they

present at present an enigmatic group which I feel must be investigated to understand the development of the modern "professional classes".

EXPERIMENTS IN LABORATORY 1805

Page

[1 2 Prussian Blue 1/5/1805 Yield measurements]

3	Mothers $\frac{1}{2}$ pint mothers	2oz	6D	0	grain above water
	$\frac{1}{2}$ pint	2	4	0	
	1 Pint	5	0	0	
	<u>per Assay bottle</u>	$\frac{24\frac{1}{2}}$			80

$\frac{1}{2}$ gallon evaporated to dryness in an iron ladle - much of it adhered so strongly thereto that it could not be got off but by warm water.

4 Troy weights:

The Troy Pound contains 5,760 grains
 The Troy Ounce contains 480 grains

Avoirdupois:

The avoirdupois ounce contains $437\frac{1}{2}$ Gr
 The ~~Ditto~~ pound contains 7000 Gr

NOTE:

1 avoirdupois ounce of salt put into an ale pint of hot water and dissolved raises the specific gravity of the water to 2/80ths of the Assay Glass.

5 Weights of Assay Glasses:

	Grains		Oz	Troy Dr	Gr
No.1	6600	or	13	6	
No.2	6020	or	12	4	20
No.3	5928	— or	12	2	48
No.4	6120	or	12	7	40
Avoirdupois:					
Glass No.1			15	1	0
" 2			13	12	
" 3			13	9	0

6 18 December 1805 Assay on Clarified Alum liquor at 12/80ths.

Glass No.2 Sett with liquor boiled to 25 including $\frac{1}{2}$ ounce of muriate of potash, this glass gave out Alum - 3.13 *†

Glass No.3 Sett as the above with $\frac{3}{4}$ ounce of muriate and yielded Alum - 4.15 *†

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Glass No.4 Sett as the above with 1 ounce muriate

and gave

- 5.10 *†

Each glass contained 1 ale pint or 35½ inches but the muriate was added in a dry state to 50 inches in the above experiments and boiled a little; the setting weights of each glass was 25/80ths.

The above results are in avoirdupois weights.

Mothers of the above. 2† say 23

7 [Set against - opp - the results asterisked]

Avoirdupois

153 Grains Muriate to the Ale Pint or 2¾ ounces per gallon

230 Grains Muriate to the Pint or 4 ounces 3 drams per gallon

306 Grains Muriate to the Pint or 5 ounces 10 drams per gallon

8 Weight of Dry Salt

- of ditto 104.5 drams

Brimstone Ashes

lb	oz	dr	
3	1	6	Dried Brimstone Ashes
2	13	2	Dried Elixated Ashes
	4	4	Salt

9 21 December 1805

Glass No.1 1 ale pint measure 1 ounce Muriate from Dunbar sett at 24

Glass No.2 1 ale pint measure 1 ounce Muriate from Dalmuir sett 24

Glass No.2 1 ale pint liquor 1 ounce Aldersons ashes sett 24

Glass No.4 1 ale pint liquor 1 ounce Sulphate Potash from Brimstone Ashes

10 18 January 1806

3 lbs Brimstone Ashes from London elixiated with Sundry portions of water until all the salt was extracted the ley filtred and put into an iron pot and boiled down to a dry salt.

	lb	oz	dr
Weight of the empty pot	6	10	8
Weight of the pot with the dry salt	7	1	10
Weight of dry salt in 3 lib ashes		7	12
One tone of brimstone ashes will yield dry sulphate of potash.	2	3	24

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The 3 pounds of the Brimstone Ashes used in this Experiment were dried then the sample from London

(in the $\frac{1}{2}$ lib Brimstone ashes lixiviated with one W Pint cold water Ley - $3\frac{1}{2}$ d wine pint) $\frac{1}{2}$ lib Brimstone ashes lixiviated with one W Pint hot water Ley - 4d

11 21 January 1806

No.2 Glass set at $22\frac{1}{2}$ dwt with 1 ounce of the dry sulphate of potash from the Brimstone ashes Produce 3 " 12 " 0

No.3 Glass set same as the above with 1 ounce Muriate from Dalmuir Produce 5 oz 2 Dr 0 Gr

12 20 April 1806

Put into the pan 3 Wine Gallons clarified alum liquor - which weighed when cold 14 dwt when at the boiling point it weighed 11 dwt. The liquor was H M boiled 3 40 during which time 3 gallons of liquor were consumed.

3 gallons (the quantity at first) was set to crystallise at 24 dwt & no Muriate added nor any other Alkali.

Mothers 22d decanted off the alum & the Alum washed weight of the Mothers cold 26dwt in cooling and crystallising the decrease was 4 gallons nearly.

The Mothers 23d boiled again and sett at 26 to crystallise.

13 Produce from the first crystallisation 2 lb 0 oz 12 dr after the alum had been washed and allowed to drain 15 hours.

14 - 25

26

Temp 50°

Assay Bottle 80 parts	Assay Bottle <u>100</u> parts 12gr	Specific Gravity	Hydrometer
9	$11\frac{1}{3}$	1.108	23
$9\frac{1}{4}$		1.115	
$9\frac{1}{2}$		1.118	
$9\frac{3}{4}$	$12\frac{1}{4}$	1.120	25
10	$12\frac{1}{2}$	1.125	26

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10 $\frac{1}{4}$		1.128	
10 $\frac{1}{2}$	13 $\frac{1}{4}$	1.130	26 $\frac{1}{2}$
10 $\frac{3}{4}$		1.134	
11 $\frac{1}{4}$	14 $\frac{1}{4}$		28
11		Divide the Specific Gravity by 16 gives the avoirdupois pounds in the Cubic Foot	
13	16 $\frac{1}{4}$		

There is 15 grains in each Dwt of the assay bottle Multiply each Dwt by 15 to which add 1200 Grains being the weight of the water, divide the sum total by the number of Grains that gives the specific gravity, add cyphers to the dividend until you get 4 figures in new Quotient prick off new Left Hand figure for the interger.

Empty Alum Assay bottle	1590 Grains
Container of Water	<u>1200</u> Grains
Oz Dr Gr	
Troy 5 6 30	2790 Grains

27 Example

Pennyweights 15 grains each Dwt by
10 the weight of the (bottle)
 150

Add 1200 Grains the weight of the water the assay bottle contains

1200)1350000	(1.125	Specific Gravity which is about 26 by the hydrometer.
<u>12</u>		Nearly 26 by the hydrometer
150		Multiply by 5
<u>120</u>		1 @ 130
3000		and add the interger
<u>2400</u>		
6000		
6000		

[28 Similar but not annotated in calculations.]

LITERATURE REFERENCES

In these references the following abbreviations are used:-

BB refers to items in the Baker-Baker Collection held in the Department of Palaeography, University of Durham.

ZNK refers to the Zetland (Dundas) Collection held in North Yorkshire County Record Office, Northallerton.

- 1 Lavoisier A L translated Robert Kerr "Elements of Chemistry" Edinburgh 1790, facsimile edition New York 1965 with introduction by Douglas McKie. The original English translation was published to meet the beginning of the Edinburgh University session of 1790. However McKie points out that Lavoisier had begun to attack the Phlogiston Theory about 1782 (page XXII) and that Black was teaching these ideas to his students before 1784 (page XXV). One might feel that the true revolution began with the sealed note given to the secretary of the Academie Royale des Sciences on November 1st 1772 where Lavoisier reported the gain in weight on burning and the "air" recovered on subsequent reduction (page XIX), however McKie concludes (page XXIX) that the publication of the "Elements" was the conclusive step in the revolution and quotes Lavoisier as writing in 1791 that "All young chemists adopt the theory and from that I conclude that the revolution in chemistry has come to pass".
- 2 See Multhaus Robert P ^{Technology ~ Culture 12 p 163} "The French Crash Program for Saltpetre Production" and Gillespie C C "The Natural History of Industry" Isis Vol 48 (1957) pp 398-407.
- 3 Berthollet trans W Hamilton MD "Elements of the Art of Dyeing" 2 vols London 1791.
- 4 de Charmes Pajot "The Art of Bleaching Piece Goods, Cottons and Threads of every description" London 1799.
- 5 Chaptal M J A "Chemistry Applied to the Arts and Manufactures" London 1807 4 vols.
- 6 Clement and Desormes "Theory of the Fabrication of Sulphuric Acid" appeared in Nicholson Journal vol 17 (1807) page 41
- 7 See page 133 below and article of Farrar W V, Farrar K R and Scott E L "The Henry's of Manchester, part 4 - William Henry and the Gas Industry" Ambix vol 22 pp 186-204.
- 8 Henry W "On the Analysis of British and Foreign Salt" Phil Trans vol 100 (1810) pp 89-122
- 9 Watson William "A Guide to the Guisborough Alum Works" Stokesley 1854 p 37
- 10 Hardie D W F & Pratt J Davidson "A History of the Modern British Chemical Industry" London 1966 page 4
- 11 de Reaumur Monsieur "L' Art de convertir le fer forge en Acier et L' Art d'adoucir le fer fondu" Paris 1722. See also Gibbs F W "A Note Book of William Lewis and Alexander Chisolm" Annals of Science vol 8 pp 202-220 for evidence of primitive "process control" in iron works.
- 12 See page 119 below

- 13 See page 120 below.
- 14 Lock A G & C G "A Practical Treatise on the Manufacture of Sulphuric Acid" London 1879 page 145 - "The Governor".
- 15 Clegg Samuel Jun "A Practical Treatise on the Manufacture and Distribution of Coal Gas" London 1841 see p 78.
- 16 Solla Price D J "Is Technology Historically Independent of Science" Technology and Culture vol 6 (1965) No.4.
- 17 Multhaus Robert P "The Origins of Chemistry" London 1966
- 18 Clow A and N "The Chemical Revolution" London 1952
- 19 Musson A E and Robinson E "Science and Technology in the Industrial Revolution" Manchester 1969
- 20 Taylor Francis Sherwood "A History of Industrial Chemistry" London 1957
- 21 Musson and Robinson op.cit reference 19 especially pages 292-298
- 22 Clow op.cit reference 18 page 187; also Musson and Robinson op.cit reference 19 page 256-7.
- 23 Musson and Robinson op.cit reference 19 page 261
- 24 See Buchanan R A "Industrial Archeology in Britain" London 1972 but many other books and a series of regularly issued journals - both national and regional - demonstrate the rapid development of this subject. The Bibliography gives more examples.
- 25 Logan J C "The Operation of a Glass Works in the Industrial Revolution" Industrial Archeology vol 9 No.2 1972
- 26 Holmyard Singer Hall & Williams editors "A History of Technology" vol IV Chapter 8 p 214 section 1). Holmyard "Development in Chemical Theory and Practice" section 2) Clow A "Interaction with Industrial Revolution".
- 27 Derry T K and Williams T I "A Short History of Technology" Oxford 1960 p 703 give a brief note on the early Objectives of The Royal Society.
- 28 Williams T I ed "A Biographical Dictionary of Scientists" London 1969 p 436
- 29 Chaptal M J A op cit reference 5 and see pages 108 and 109 below.
- 30 Higgins Bryan "Observations and Advice for the Improvement of the Manufacture of Muscavado Sugar and Rum" London 1797
- 31 Clow op cit reference 22 page 79
- 32 ZNK VII 2,164 Recommendations copied on page 1 of this ["]Book of Experiments 1829. Some of the recommendations followed up systematically with planned experiments.
- 33 ZNK VII 2,162 "Experiments in Laboratory 1805"
- 34 ZNK VII 2,166-71 a series of letters from Alex Tod reporting investigations 1830-31

- 35 BB 7/557 Pay Ledger D for example names liquormen and other employees with their rates of pay. However except for the case of a death, no other information is given.
- 36 See pages 54 and 68 below
- 37 See the accounts of Ure and Knapp on Alum Manufacture commencing pages 77 and 85 below.
- 38 BB 3/413
- 39 ZNK X 1, 2, 310 a letter of December 2nd 1777 from Sir Thomas Dundas to Sir Lawrence Dundas
- 40 BB 7/560 "Copy of Letters Book D" page 333 a letter to Mrs Baker May 3rd 1793 see postscript.
- 41 Op cit reference 38 see also page 9
- 42 ZNK X 1, 2, 650 first letter dated July 26th 1788
- 43 Clow A and N op cit reference 18
- 44 Taylor F S op cit reference 20
- 45 Ibid page 167-171
- 46 Ibid
- 47 Gibbs F W quoted by Musson in his Editors Introduction to "Science Technology and Economic Growth in the Eighteenth Century" edited A E Musson, London 1972 page 58
- 48 Daumas M "The Extraction of Chemical Products" which is chapter 10 of "A History of Technology and Invention" edited by M Daumas and published in translation New York 1969 - pages 172-211
- 49 "Diderot's Encyclopaedia" has now been reprinted, translated and annotated by C C Gillispie
- 50 Gillispie C C "The Natural History of Industry" originally ISIS Vol 48 (1957) reprinted in "Science of Technology in the Eighteenth Century" ed Musson, op cit reference 47
- 51 Ibid page 131
- 52 Ibid page 131
- 53 Ibid page 134
- 54 Court Susan "The 'Annales de Chimie' 1789-1815" ~~Ambir~~ vol 19 pp 113-128
- 55 Gibbs F W "William Lewis (1708-1781)" Annals of Science vol 8 pp 122-151
- 56 Rancke Madsen E "The Development of Titrimetric Analysis till 1806" Copenhagen 1958
- 57 Schofield R E "Josiah Wedgewood Industrial Chemist" Chymia vol 5 p 1801
- 58 Musson A E editor "Science Technology in the Eighteenth Century" op cit reference 47, see Editors Introduction p57

- 59 See presidential address of Dr R Nichollis to Coke Oven Managers' Association to be delivered November 1977.
- 60 Ibid and personal experience.
- 61 Derry T K and Williams T I "A Short History of Technology" Oxford 1960 p 322
- 62 Banned from Loftus see ZNK X, 1, 2, 1247 also Clow op cit reference 18 pp 402-423
- 63 Lock and Lock op cit reference 14 (title page)
- 64 Cross referencing in Ure and Knapp's Alum accounts to other sections of their Dictionaries op cit references 282 and 286
- 65 Buchanan Robertson "The Economy of Fuel" Glasgow 1815
- 66 Forbes R J "The Invention of ^{the} Rectifying Column" Trans Newcomen Society vol 26 p 105
- 67 Dickenson H W "The Utilisation of Waste Heat from Industrial Operations" Trans Newcomen Society vol 24 page 1
- 68 At one point Boulby had insufficient roasted ore to continue operations see below page 46
- 69 Mainly waste of steam, visible to anyone passing a major chemical works
- 70 See pages 62-69
- 71 For attempts to utilise or recycle the waste Burnt Lime in alum works op cit reference 34 and page 54 below. For wide ranging views on waste utilisation see Simmonds P L "Waste Products and Undeveloped Substances" London 1873
- 72 Op cit reference 59 and also G Lunge paper in "Proceedings of Tyne Chemical Society" "Analytical Methods for Alkali Works" December 1875
- 73 A study on the development of Thermostats has been made by Ramsey A K J "The Thermostat or Heat Governor - an outline of its history" Trans Newcomen Society vol 25 p 53
- 74 Op cit reference 33 and also ZNK VII 3, 4, 4. "Stock Book 1827" p 16 refers to "Laboratory" and gives the value of the Chemicals and Utensils as £48.10.
- 75 Op cit reference 32, 33, 34
- 76 Turton R B "The Alum Farm" Whitby 1938 p 105
- 77 Parkes Samuel "Chemical Essays relating to the Arts and Manufactures of the British Dominions" 5 vols London 1815 - second edition in 2 vols 1823
- 78 For example; Black see Clow op cit reference 18 p 79; Dalton p 144 Faraday op cit reference 32 above
- 79 Russell C A, Coley N G and Roberts G K "Chemists by Profession" Milton Keynes 1977
- 80 See work of Henry p 133 below; Accum⁽¹⁸¹⁹⁾ pages 140-143

- 81 Gray Malcolm "The Kelp Industry in the Highlands and Islands" Economic History Review Second Series vol 4, p 197.
- 82 Smith J G "Studies of Certain Chemical Industries in Revolutionary and Napoleonic France" Ph D Thesis University of Leeds 1969
- 83 Often negative see Alum exports pages 95 and 96 but also note action of privateers page 59
- 84 See page 118 but note also Thos Newbigging and W T Fewtrell eds "Kings Treatise on the Science and Practice of the Manufacture and Distribution of Coal Gas" London 1878 pp 63 and 64 explaining how Hill made £100,000 in 14 years of litigation
- 85 Ibid especially Roebuck's ineffective attempts to protect his patent see p 119
- 86 Note references to high walls around Roebuck's Prestonpans plant p 119 below
- 87 In the case of alum due to close knit "managerial group" see "Account of Participants" and in the case of sulphuric acid due to scientific interest page 1
- 88 See page 97
- 89 Spence Peter for biographical details see Clow op cit reference 18 pp 243-244
- 90 Turton op cit reference 76
- 91 Singer C "The Earliest Chemical Industry" London 1948
- 92 Watson op cit reference 9 p37
- 93 Dictionary of National Biography, vol VI p 880
- 94 Colwall D "An Account of the English Alum Works" Phil Trans vol XII 1678 pp 1052-1056
- 95 Turton op cit reference 76 p 102
- 96 Ibid p 102
- 97 Ibid p 103
- 98 Colwall op cit reference 94 p 1053
- 99 Turton op cit reference 76 p 104
- 100 Colwall op cit reference 94 p 1053
- 101 Ibid p 1053
- 102 Singer C op cit reference 91 p
- 103 Colwall op cit reference 94 p 1055
- 104 Ibid p 1055
- 105 Ibid p 1055

- 106 Turton op cit reference 76 p 105
- 107 See page 54 below
- 108 Colwall op cit reference 94 p 1055
- 109 Ibid p 1055 see also Watson op cit reference 9 for details of collection p 88
- 110 Watson op cit reference 9 p 20
- 111 Chaptal op cit reference 5 . First published in French as "Chimie appliquee aux Arts" published Paris 1803
- 112 Williams op cit reference 61 p 104
- 113 Chaptal op cit reference 111
- 114 Chaptal M J A "On the Method of making Alum by the direct Combination of its constituent Principles" Reparatory of Arts vol 2 (1795) p 134
- 115 Chaptal op cit reference 5 vol 4 pp 39 -77
- 116 Beaume's aerometer or hydrometer, still in use; for conversion table see Speirs H M "Technical Dates on Fuel" London 1950 p 36
- 117 Winter R "A Mineralogical Outline of the District containing the Aluminous Schistus in the County of York with the entire Process practiced in the Manufactory of Alum to which is added an Analysis of the Sulphate of Alumina and the Super Sulphate of Alumina and Potash with practical observations and Remarks" Nicholson's Journal vol 25 (1810) p 241
- 118 Colwall op cit reference 94 p 1052
- 119 Winter op cit reference 117 p 247 gives details of analysis
- 120 Graves Rev J "History of Cleveland" Carlisle 1808 pp 335-6
- 121 Winter op cit reference 117 p 248
- 122 Letter from George Dodds to Mrs Judith Baker BB 7/559 "Letter Book C" p 175
- 123 Young Rev George "History of Whitby" 2 volumes, these acknowledgments are found in vol 2 p 817
- 124 Ibid this account can be found in vol 2 pp 811-815
- 125 Ibid vol 2 pp 810-811
- 126 "Cleveland Industrial Archaeologist" No 2 (1975) Published by The Cleveland Industrial Archaeology Society
- 127 BB 2/210 "Enquiries about the All^o Trade" contained in a booklet
- 128 Ibid
- 129 See Pay Ledgers in Records for job titles BB 7/557 "Pay Ledger D" also gives remuneration

- 130 ZNK X, 1, 2, 398 Letter or report to Sir Lawrence Dundas dated September 4th 1781
- 131 See pages 8, 39, 54, 60, 62, 63
- 132 BB 1/5 Letter of May 14th 1743
- 133 See "Ralph Ward's Journal" Yorkshire Archaeological Society vol 67 (1951)
- 134 Graves op cit reference 120 p 332
- 135 BB 1/7 Letter from Thomas Wardell to George Baker December 14th 1754 concerning organisation of the plant and alum sales etc
- 136 Wardell died July 6th (BB 1/107b). See BB 1/99 for last letter dated June 21st, His widow was still receiving an annuity from the partnership of Baker and Jackson in 1811 - last record £10 for half year paid on May 31st 1811 and recorded on page 159 of Pay Ledger D (BB 7/557).
- 137 BB 1/100 is reproduced as page 41
- 138 BB 1/16 Letter of August 8th 1754 from Thomas Wardell to *Geo. Baker*
- 139 ZNK VII 5, 1 p 242 of a letter book of William Usher 1803-1811; letter of 4-1-1809; last relevant reference is on p 366 where a payment is made to Dodds (14-5-1810)
- 140 Young op cit reference 123 vol 2 p 947
- 141 Baines *Directory 1823* p 416 but note that Pay Ledger D (BB 7/557) gives him as clerk in 1807 (*see Bibliography for full title*)
- 142 BB 19136 but he appears as agent throughout Pay Ledger D (BB 7/557) although there is no reference to his son
- 143 Op cit reference 141 p 416
- 144 ZNK VII 2/166-171
- 145 White W "History, Gazetteer and Directory of the East and North Ridings of Yorkshire" Sheffield 1840 p 667
- 146 ZNK VI 4, 2
- 147 ZNK VI 4, 2 letter to Mr Baker Baker - not Forster - dated February 2nd 1869
- 148 ZNK X 1, 2, 100-137 Letters from August 24th 1766 to September 10th 1769
- 149 ZNK X 1, 2, 552 Letters to James Farquharson dated March 23rd 1785
- 150 ZNK X 1, 2, 498 Letter of James Farquharson dated February 16th 1783
- 151 Op cit references *41 and 42* above. See pages 8 and 9 above
- 152 ZNK X 1, 2, 1247 Last letter dated November 20th 1794 first letter as agent ZNK X 1, 2, 650 dated July 26th 1788

- 153 ZNK X 1, 2, 345 and ZNK X 1, 2, 462 dated February 20th 1782 and May 20th 1782
- 154 ZNK X 1, 2, 1391 dated September 14th 1802
- 155 ZNK X 1, 2, 1623 letter dated March 18th 1807; also letter books ZNK VII 5, 1 and 2 letter books 1803-15; the 1816 letter written by Tod ZNK X 1, 2, 2084
- 156 ZNK X 1, 2, 2081 and 2082 letters of 16th and 18th March 1816
- 157 ZNK X 1, 2, 2080;
- 158 ZNK VII 2, 166-71
- 159 Baines op cit reference 141
- 160 ~~Op cit reference 144~~ Pigot's Directory 1834
- 161 White op cit reference 145 p 164
- 162 See below p 73
- 163 BB 2/190
- 164 BB 2/212
- 165 See above p 34
- 166 BB 2/323b
- 167 White op cit reference 145 p 683
- 168 Young op cit reference 123 p 649
- 169 BB 1/7 letter of Thomas Wardell to George Baker dated December 14th 1742
- 170 BB 2/190
- 171 BB 2/212
- 172 BB 7/559 p 175 letter to Mrs Baker
- 173 ZNK X 1, 2, 1247
- 174 Op cit reference 172
- 175 BB 7/559 p 255
- 176 Ibid p 252
- 177 BB Ibid p 278
- 178 BB Ibid p 285
- 179 BB 3/434
- 180 BB Ibid
- 181 BB 2/220. The major inventory of 1776 (BB 1/147) gives full details of these items of equipment.

- 182 ZNK VII 2, 164
- 183 Winter op cit reference 117 p 250
- 184 BB 3/345
- 185 BB 2/337b
- 186 See p 21
- 187 BB 3/347a
- 188 Op cit reference 126 p 33
- 189 ZNK VII 2, 162 "Experiments in Laboratory 1805"
- 190 Turton op cit reference ⁷⁶ p 104-5
- 191 Watson op cit reference ⁹ p 76
- 192 Ure "Recent Improvements 1845" pp 5-6
- 193 In the event this can be dealt with here. Twaddel or Twaddle, a Glasgow instrument maker made a pocket "deorometer" for use of the workmen in collecting urine for the elder Mackintosh's ammonia stills in the 1770s. See Clow op cit reference 18 pp 211-2
- 194 ZNK VII 2, 166-171 Letter of September 3rd 1830 where he "suggests the use of exhausted may be beneficial"
- 195 Ibid. The first part of the letter describes the experiments
- 196 Ibid
- 197 Ibid
- 198 See Inventories (ZNK VII 3, 4, 4) from 1827 for laboratories and also for record of chemical library including Thompson, Accum, Henry, Chaptal, Parkes as early as 1820 (ZNK VII 3, 4, 3 pp 17-18
- 199 Watson op cit reference ⁹ pp 17-20
- 200 Op cit reference 126 p 31
- 201 BB 2/239
- 202 BB 2/307b
- 203 BB *ibid*
- 204 Op cit reference 126 p 32
- 205 Chapman S K "Excavations at the Boulby Alum Works" op cit reference 126 p 32
- 206 See pages 79-80 and pages 87-8
- 207 Op cit reference 126 p 33

- 208 BB 2/239
- 209 ZNK VII 2, 163 "Report upon the New Process of Alum". However one must not overlook the point that this may be one of the innovations making the technique "new". On the other hand see the account of the Scottish process below.
- 210 Watson op cit reference 9 p 88
- 211 BB 7/561
- 212 Gray op cit reference 81 and Clow op cit reference 18 pp 79-82 are two good examples.
- 213 Gray op cit reference 81
- 213a ZNK X 1, 2, 372 letter dated June 26th 1781
- 214 BB 7/559 Letter Book C page 2 letter of September 12th 1778. The following letter of September 18th on page 2 gives 57 tons.
- 215 BB 7/559 Enemy squadrons moving up coast page 165 - progress reports.
- 216 BB 2/192
- 217 Clow op cit reference 18 p 74
- 218 BB 7/559 p 3
- 219 BB 7/559 p 166 letter of September 25th 1779
- 220 BB 1/106
- 221 BB Ibid
- 222 BB Ibid
- 223 BB 1/107a
- 224 BB 7/559 page 140 Letter to Mistress Dorothy Creswell
- 225 BB 2/220
- 226 BB 3/436 reproduced as page 61
- 227 BB 7/559 page 256
- 228 BB 7/559 page 258 Letter to Mrs Judith Baker March 4th 1780.
- 229 BB 7/559 page 277 Letter from George Dodds to Mrs Judith Baker April 22nd 1780
- 230 BB 2/210
- 231 BB 2/210 footnote to above table
- 232 BB 7/559 page 290
- 233 BB 2/210 abstracted from table of "Enquiries" op cit reference 230
- 234 Hodgson G "History of South Shields" Newcastle 1903 pages 359-63 also in alum touched at S. Shields page 359

- 235 BB 7/559 page 151 Letter of September 4th 1779
- 236 BB Ibid page 341 Letter of September 23rd 1780. The British Barilla used at Cookson's works.
- 237 BB 3/403
- 238 BB 3/404
- 239 BB Averages from the Manager's Monthly reports for that year.
- 240 BB 3/466 note dated October 25th 1787
- 241 ZNK VII 5, 1 page 243 dated January 4th 1809
- 242 ZNK X 1, 2, 1398
- 243 Graves op cit reference 120 p 347
- 244 Ibid
- 245 BB 3/544
- 246 Welford R "Men of Mark 'Twixt Tyne and Tweed" London 1895 vol 3 pp 92-97
- 247 Robinson E "Training Captains of Industry "Annals of Science vol 10 pp 301-313
- 248 Op cit reference 246; see also Clow op cit reference 18 p 100 where Dundonald features as moving force
- 249 Armstrong, Bell I, Lowthian; Taylor; Richardson; editors "Industrial Resources of the Tyne, Wear and Tees "British Association for the Advancement of Science London 1864 p 158
- 250 ZNK VII 5, 1 page 174
- 251 BB 3/404
- 252 ZNK VII 5, 1 page 171 dated December 25th 1807
- 253 ZNK VII 5, 1 page 364
- 254 ZNK VII 5, 2 "Letter Book of William Usher 1811-1815" page 71; letter dated August 31st 1812
- 255 Watson W op cit reference 9 p 39
- 256 Ibid page 39
- 257 Ibid pp 70-74
- 258 Ibid
- 259 In by-product recovery and gas purification techniques on most modern carbonisation plants.
- 260 Op cit reference 257
- 261 Op cit reference 249 p 171 Potash alum made at Loftus

- 262 BB 2/215. Managers' report for May 1782. Entry for May 11th.
- 263 BB 2/236. Manager's report for March 1783. Entry for March 27th.
- 264 BB 2/240. Manager's report for April 1783. Memorandum
- 265 Based on the analyses quoted by Gittens L. "The Manufacture of Alkali in Britain 1779-1789" *Annals of Science* vol 23 (1966) p 175
- 266 No entry under this number.
- 267 See page 63
- 268 BB 6/556 p 47
- 269 BB 7/559 p 236 Letter to Mrs Baker dated January 15th 1780
- 270 ZNK VII 2, 163 See also page 105 for Scottish practice
- 271 Ibid ZNK VII 2, 163
- 272 "Industrial Celebrities V, Peter Spence "The Chemical Trade Journal," January 4th 1890 p 9
- 273 ZNK VII 2, 163
- 274 Ure op cit reference ¹⁹² pp 5-6 gives full list of liquors
- 275 Watson op cit reference 9 p 56
- 276 Buchanan, Robertson op cit reference 65 p 361
- 277 ZNK VII 2/166-171
- 278 Watson op cit reference 9 pp 78-9
- 279 Op cit reference 274
- 280 Winter op cit reference 117 p 249
- 281 Ibid pp 253-4
- 282 Ure A "Dictionary of Arts, Manufactures and Mines" London 1839
- 283 4th Edition 1853 (2 vols); 5th Edition 1861 (3 vols) enlarged ed R. Hunt; 6th Edition 1867 R Hunt; 7th Edition 1875 (4 vols) ed R Hunt and F W Rudler
- 284 See page 73
- 285 Op cit reference 282. The Account of the alum manufacture - here paraphrased is quite short and is found on pages 33 to 39.
- 285a *Thenard and Roard. Memoir a Roman Alum. Nicholson J. Dec. 1807 p 275'*
- 286 Knapp F L "Chemical Technology" translated by Dr E Ronalds and Dr T Richardson 3 vols London 1848. Vol II pp 154-179. The analysis of Sandebar is in vol II pp 33-34; The comments on Kelp are in vol I p 301.
- 287 NCB 1/SC/486 Note Book of Robert Simpson (part of "The Buddle Papers") concerning Coke Works. Coal analyses pp 32-4 by Dr T Richardson who was also one of the editors of reference 249 above. - Consulting charges - For analyses c. 1860 - given by W. F. Campbell. "A Century of Chemistry on Tyneside 1868-1968" Newcastle upon Tyne p 39

- 288 BB 3/430 is page 95 and BB 3/458 is page 96
- 289 BB 1/147 Inventory of 1776
- 290 BB 2/190 Entry for June 25th 1781 and BB 3/351 Entry for February 21st 1785.
- 291 Barton P "The Alum Ships" Dalesman March 1969
- 292 Smith op cit reference 82. p 37
- 293 Ibid p 38
- 294 Ibid p 41
- 295 Ibid p 42
- 296 BB 9/98 letter of November 17th 1746
- 297 "Ward's Journal" op cit reference 133
- 298 Pickles R L "A Brief History of the Alum Industry in North Yorkshire 1600-1875" op cit reference 126
- 299 ZNK VII 2, 26 these reproduced pages are supplemented by a list of rules and exceptions.
- 299a BB 15/25: letter from Ralph Jackson to Mrs Judith Baker: innovation in prep. of
keep less.
- 300 Turton op cit reference 76 p 107
- 301 Pickles R L op cit reference 298 p 8
- 302 Whitehead's Newcastle and Gateshead Directory for 1790 corrected to May 1790 printed D Akenhead Newcastle 1790. Reprinted R Ward and Sons and presented to the subscribers to Ward's Directory Newcastle, January 1902.
- 303 Communicated by Mr W A Campell
- 304 BB 7/559 "Copy of Letters" Book C p 160
- 305 BB Ibid p 166 letter dated September 25th 1779
- 306 BB ibid p 169
- 307 BB Ibid p 235 letter from Dodds to Mrs Judith Baker dated January 15th 1780
- 308 BB 1/147 Inventory of 1776
- 309 BB 2/206 Monthly Report of February 1782 Entry for 27th February
- 310 BB 3/429 Monthly Report of May 1786 Entry for 15th May
- 311 BB 1/106 and 1/108 and 1/109 and 1/110
- 312 BB 7/560 "Copy of Letters" Book D p 25 letter dated March 10th 1781
- 313 BB 3/514 "The Annual Account 1790-1" the other figures taken from similar accounts BB 3/478; 3/501; 3/526
- 314 BB 7/560 Letter Book D p 205 letter dated April 20th 1782

- 315 Clow op cit reference 18 p 245. Dodds tried to sell scrap iron to a Newcastle copperas plant BB 7/559 p 33
- 316 ZNK VII 3, 4, 1 p 2
- 317 Watson op cit reference 9 p 65
- 318 Ibid page 90
- 319 ZNK VII 4, 2 notes in letter book dated January 7th 1869
- 320 Clow op cit reference 18 ; p 627 gives 1797 as the year; p 239 gives details
- 321 Nicholson's Journal vol 26 (1807) p 233 "Some Account of a very singular and important Alum Mine near Glasgow at present worked by Messrs Mackintosh Knox and Co"
- 322 BB 3/539 mentioned in a letter from George Dodds to George Baker April 6th 1804
- 323 See p 78
- 324 "On the Alum Ore of Toifa"; in a letter to M Berthollet from M Gay Lussac. Reparatory of Arts vol 9, Second Series (1806) p 51
- 325 Chaptal op cit reference 114
- 326 Smith J G op cit reference 82 p 37
- 327 Ibid page 38 (Notes 326 and 7 are not direct quotation; more summaries)
- 328 Ibid p 41
- 329 Singer op cit reference 91 "The Earliest Chemical Industry" p 273
- 330 Chaptal op cit reference 5
- 331 Watson op cit reference 9 pp 42-45
- 332 Singer op cit reference 91
- 333 Ibid p 284
- 334 Hardie and Pratt op cit reference 10 p 155
- 335 Vanquelin Citizen "A Memoir on the Nature of the Alum of Commerce, on the Existence of Potash in this Salt, and on various simple or triple combinations of Alumina with the Sulphuric Acid" Nicholson's Journal vol 1 (1797) p 318
- 336 Royal Institution Archives in Facsimile, Manager's Minute III 1802-4 p 24
- 337 Winter op cit reference 117 p 254
- 338 Wilson J "Researches into the Alum Manufacture" Philosophical Magazine 4th Series vol 9 (1855) p 415
- 339 Knapp see page 87 above
- 340 This Historical survey is a summary of the accounts of W A Campbell "The Chemical Industry" Industrial Archaeology series No 7 London

1971 pp 12-25 and of Clow A and N "The Chemical Revolution" London 1952 pp 130-150. These sources provide the bulk of the information and are not quoted again in this section.

- 341 Parkes "Chemical Essays" op cit reference 77 , 1825 edition vol 1 p 468
- 342 His further travels spread the "news" to Bewdley see Parker A "Samuel Skey (1726-1800) and Chemical Industry in Bewdley" Trans Newcomen Society vol 27 pp 217-218. Parkes op cit reference 341 p 398 notes that Skey waxed opulent.
- 343 Derry and Williams "Short History of Technology" op cit reference 61 p 535
- 344 Smith J G op cit reference 82 p 4
- 345 Park W A "The Development of the Heavy Chemical Industry in West Ham and District" M.Sc Thesis (London) 1950
- 346 Smith J G op cit reference 82 , but Park op cit reference 345 disagrees.
- 347 Smith J G op cit reference 82
- 348 Park op cit reference 345. He notes that B.A.S.F. workers Kneitsch and Krauss investigated the reversible oxidation of sulphur dioxide and found that:
- (1) the best working temperature was 450°
 - (2) the trioxide yield increased with increased oxygen concentration but dilution with atmospheric nitrogen reduced yield
 - (3) maximum working yield of 99% conversion achieved with 15 volumes of air to one volume sulphur dioxide cf 91% with stoichiometric proportions
 - (4) iron (iii) oxide and arsenic salts poisoned the catalysts
- 349 *Campbell (1971) p22.*
- 350 Clow op cit reference 340 p 132
- 351 Campbell op cit reference 340 p 14
- 352 Ibid This process is given also in Parkes "Chemical Catechism" 1819 p 147 footnote no d , however he describes the quantity of water as indeterminate and gives the target concentration as S.G. 1.845
- 353 Ibid. The construction details are contained in Parkes "Chemical Essays" op cit reference 77
- 354 *Parkes op. cit ref. 341*
- 355 Clow op cit reference 340 p 145
- 356 Campbell op cit reference 340 p 16
- 357 Park op cit reference 345
- 358 Smith J G op cit reference 82

- 359 Ibid
- 360 Lock and Lock op cit reference 14 pages 4-40
- 361 Smith H A "The Chemistry of Sulphuric Acid Manufacture" London 1873. The Lock and Lock analyses are abstracted from those of Smith who was a works chemist in an alkali works page
- 362 Ibid. All the methods quoted are to be found in Smith's monograph pages 15-21. In the use of sodium chloride page 18 at which the Locks wax sarcastic explains the problems and concludes "This plan was then thrown aside". Smith's work is also interesting in his concern for the dangers of environmental pollution by arsenious compounds produced by the process. However the author's modest conclusion that he had "brought together facts which, scattered though some of them are and comparatively insignificant, yet are of great value to manufacturers of sulphuric acid" inspired a disgruntled reader of the copy kept in the library of the Literary and Philosophical Society of Newcastle upon Tyne to underline the word "insignificant" and made the marginal annotation "very". Certainly both Smith's and the Lock's books were quickly eclipsed by the massive and definitive work of George Lunge on "Sulphuric acid and Alkali" whose first edition was published around 1880.
- 363 Lock and Lock op cit reference 14. The bulk of the information quoted in the remainder of this section is taken from this work and it will not therefore be cited again.
- 365 Smith op cit reference 82. The second section of the monograph seems to do for the sulphuric acid manufacture what Wilson's researches did for Alum. It is worth reading the full account of his investigations on pages 22-73 of this small monograph.
- 366 Park op cit reference 345
- 367 Ibid
- 368 Campbell op cit reference 340 pp 18-19
- 369 These pans were made of lead but as Parkes comments, in Essay VII of his "Chemical Essays" op cit reference 77, the boiling point of the acid increases with concentration until it reaches the melting point of lead. In any case the acid would dissolve the lead at such concentrations.
- 370 Campbell op cit reference 340 p 19
- 371 Smith J G op cit reference 82
- 372 Campbell op cit reference 340 pp 19-20
- 373 Clow op cit reference 340 p 42 6
- 374 Elton A "The Rise of the Gas Industry in England and France". Archives Internationales d'Histoire des Sciences vol 5 p 320
- 375 Clow op cit reference 340 pp 427-429
- 376 Elton op cit reference 374
- 377 Clow op cit reference 340 p 427

- 378 Baily J "General View of the Agriculture of the County of Durham" London 1810, reprinted Newcastle 1972 pp 290-292. Baily was Dixon's nephew and recalled the experiments as boyhood memories.. He points out that Dixon used the Tar produced which he transported to Sunderland for use on ships' bottoms. The trade amounted to 6 barrels per week during the years 1779-83, after which increased transport costs made it unprofitable.
- 379 Clow op cit reference 340 p 429. Elton op cit reference 376 gives a fairer picture as does Wigginton R "Coal Carbonisation" London 1929 p 13. The latter author gives more of these early examples pp 9-15.
- 380 Clegg S Jnr "Coal Gas Manufacture" op cit reference 14 p 5. He gives a diagram of the apparatus on pp 6-7
- 381 Wigginton op cit reference 379 p 15-16 and Clow op cit reference 340 p 429
- 382 Clegg op cit reference 15 p 6
- 383 Clow op cit reference 340 p 429, the plan is reproduced as a plate opposite p 401
- 384 Clegg op cit reference 15 p 6
- 385 Ibid pages 6-8 also Hughes S "Treatise on Gas Works" ^{London} 1853 p 13 and Chapter 5
- 386 Accum F "Treatise on Gas Light" London 1819 pp 51-59
- 387 Clegg op cit reference 15 p 8
- 388 Clow op cit reference 340 pp 429-50
- 389 Elton op cit reference 374
- 390 Buckley W and McCulloch A "Leaves from an Old Notebook. A Record of Some Early Experiments on the Carbonisation of Oil and Coal by Dr W Henry F.R.S. (1808-24)" Manchester Lit and Phil Soc Memoirs. The note of this source occurs as footnote 5 to page 248 of Musson A E and Robinson E "Science and Technology in the Industrial Revolution", London 1969.
- 391 Henry W "On the aeriform compounds of Charcoal and Hydrogen; with an account of some additional experiments in the Gases from Oil and Coal" Phil Trans (1821) pp 136-61
- 392 Van Krevelen D W and Schuyer J "Coal Science" London 1957 pp 61, 69 etc
- 393 Musson A E and Robinson E op cit reference 391 pp 99-100
- 394 Clow op cit reference 340 p 430 gives Creighton as responsible for the investigations results quoted here which were the basis of the "1805 paper" below. Creighton is further mentioned on page 608 as providing an article for Encyclopaedia Britannica on "Gas Lights"
- 395 Ibid page 429
- 396 Clegg op cit reference 15 p 8 Clegg does not believe that lime purifiers were used

- 397 Ibid the paper is copied in full on pp 8-13
- 398 Clow op cit reference 394
- 399 Ibid p 429
- 400 Clegg op cit reference 15 p 13
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