

EU ENVIRONMENT PROGRAMME

Fluoride Emission Abatement in Heavy Clay Products Manufacture by Process Modification and Control

Part A: Summary

EU number: EV5V CT940526 (DGXII SOLS)



British Ceramic Research Ltd UK



TNO Institute of Applied Physics, Ceramics Division NL



FORBAIRT, Ceramics Research Unit IR

**EUROPEAN COMMISSION DIRECTORATE
GENERAL X11 SCIENCE RESEARCH
DEVELOPMENT**

**PROGRAMME
ENVIRONMENT 1991-1994 RESEARCH AREA II-2**

**CONTRACT
EV5V CT94 0526**

**FLUORIDE EMISSION ABATEMENT IN HEAVY
CLAY PRODUCTS MANUFACTURE BY PROCESS
MODIFICATION AND CONTROL**

DRAFT

PART A

SUMMARY REPORT

**PARTNERS:
BRITISH CERAMIC RESEARCH LTD, UK
TNO, THE NETHERLANDS
FORBAIRT, IRELAND**

EV5V CT94 0526

DRAFT

REPORT - PARTS A&B - SUMMARY

AUTHORS

W M CHURCHILL BSc FIM

J P FIFER BSc MIM

A H deVRIES

Ir J A M DENISSEN

T C KELLY BSc MSc Tech PhD MIE

A H M O'RIORDAN B Eng MSc

C O N T E N T S

Chapter S1 Aims and objectives of the project

Chapter S2 Introduction and partners

- S2.1 Partners
- S2.2 Management

Chapter S3 Work Plan Projected and Achieved

- S3.1 Task A Reduction of Fluoride Emission by Process Optimisation
- S3.2 Task B Mineralogical and Chemical Analysis of the Raw Materials
- S3.3 Task C Survey of Fluoride Emission Abatement Additives
- S3.4 Task D On-line Abatement Process Control
- S3.5 Task E Safe Disposal of Waste from Dry Limestone Flue Gas Scrubbers
- S3.6 Summary

Chapter S4 Results Summary

- S4.1 Initial Trials
 - S4.1.1 TNO Pilot Trials
 - S4.1.2 CERAM Research Pilot Trials
- S4.2 Industrial Trials and Emission Monitoring
 - S4.2.1 Kiln Schedule and Peak Temperature
 - S4.2.2 Limestone Addition to the Raw Material
 - S4.2.3 Effect of Oxidation and Reducing Conditions in the Kiln on Fluoride Emissions
 - S4.2.4 Setting Geometry
 - S4.2.5 Hydrogen Fluoride Concentration Profile in a Kiln and Kiln Draught
 - S4.2.6 Reabsorption of Fluoride
- S4.3 Mineralogical and Chemical Analyses of Raw Materials used in this Project
 - S4.3.1 Mineralogical Analyses
 - S4.3.2 Chemical Analyses
 - S4.3.3 Fluoride Content Determinations
 - S4.3.4 Vitrification Characteristics of the Raw Materials
- S4.4 Mechanism of Fluoride Release
 - S4.4.1 Fluorine in Clay Mineral
 - S4.4.2 Fluorine Release
- S4.5 Fluoride Abatement Additives
 - S4.5.1 Fluoride Reactive Compounds
 - S4.5.2 Fluxes
 - S4.5.3 Inert Diluents
- S4.6 Dry Limestone Exhaust Gas Scrubber Control System
 - S4.6.1 Control System Operation
 - S4.6.2 Trial Results
- S4.7 Safe Disposal of Waste from Dry Limestone Flue Gas Scrubbers

- S4.7.1 Mineralogical and Chemical Analysis
- S4.7.2 Leachate Testing
- S4.7.3 Dry Limestone Scrubber Waste Disposal by Recycling
- S4.7.4 Re-use in the Heavy Clay Industry

Chapter S.5 Conclusions

Acknowledgements

CHAPTER S1

AIMS AND OBJECTIVES OF THE PROJECT

This project was undertaken as part of the programme Environment 1991-94 Research Area II.2 Cleaner Technology, Emission Abatement Technology, Recycling Technology of the European Commission Directorate General XII Science, Research and Development.

The aim of the project was to reduce fluoride emissions to the atmosphere from the firing of heavy clay products by process optimisation and control, to develop a control system to ensure the most efficient operation of end-of-pipe abatement technology, dry flue gas scrubbers and to suggest a safe disposal route for the waste from such scrubbers.

In order to achieve the aim four primary objectives were set.

S1.1 The main one was fluoride abatement by process optimisation. This was intended to produce an inventory of low investment process modifications to enable manufacturers to reduce their fluoride emissions by at least 25% without changing the properties of products beyond the industries current tolerance limits. The identified modifications were to be applied to existing manufacturing processes and their efficacy monitored. In addition the data obtained from this objective should provide information on the design and operation of new kilns for the industry.

S1.2 The second objective was to carry out a survey of suitable additives that can be incorporated into the raw materials used in the industry that will enable significant fluoride reduction whilst at the same time noting the effects of these additives on the quality of the finished product.

S1.3 The third objective was to produce a pre-production specification for an electronic on-line monitoring and control system to operate the mechanical systems of a dry limestone flue gas scrubber for optimum efficiency, based upon a continuous fluoride analyser measuring fluoride levels at the exit of such a scrubber.

S1.4 The fourth objective was to investigate the chemical reactivity and safe disposal of waste from dry limestone flue gas scrubbers including the possible recycling of the waste material.

The whole concept behind the programme was the investigation of hitherto largely laboratory proven parameters on fluoride emission reduction in the industrial situation. At the same time address some of the consequent environmental implications.

CHAPTER S2

INTRODUCTION AND PARTNERS

Increasing awareness of the environment world wide and particularly in Europe had given rise to legislation requiring industry to minimise or preferably stop polluting it. In the European Union this legislation impacted upon the heavy clay industry in such a way that it required them to control atmospheric pollution from kiln exhausts and in particular set stringent limits on fluoride emissions. Whilst the fluoride limits laid down varied somewhat from country to country, all were set below the levels then being emitted.

In the U.K. the Environmental Protection Act sets a limit of 10mgm^{-3} referenced to STP and 18% oxygen. This limit applies to new plant, existing plant must comply with it by 31st December 1999. In the Netherlands there is no national regulation, the environmental limits are determined by local authorities. However, in 1992 the Ministry of Environmental Affairs published the "Dutch Emissions Guide" (NER) in an attempt to help local authorities frame regulations and to attain consistent limits in the Netherlands. For fluorides the NER states a general emission limit of 5mgm^{-3} referenced to 18% oxygen if the untreated emission is over 50gh^{-1} . Where a flue gas scrubber is used an emission below 5mgm^{-3} will be expected. In Ireland the concentration limit values for fluoride (expressed as HF) emission to air is 10mgm^{-3} at STP and 18% oxygen when achieved by process control without abatement equipment and 5mgm^{-3} where such equipment is installed.

To comply with the limits the industry was going to incur additional capital and operational costs which appeared particularly onerous for an industry commanding a very low selling price in terms of monetary units per kilogramme of product when compared with most if not all other industries. Industry in the Netherlands, Ireland and the United Kingdom therefore were seeking the lowest possible cost option from their research advisors. There was a two pronged approach to their request, could the existing processes be modified to minimise fluoride emissions and if exhaust gas scrubbing had to be undertaken could their operation be made as efficient as possible and the problems of the solid waste resulting and its disposal be considered.

The whole programme of the project was planned as a cooperative venture between industry and industrial research organisations that served the heavy clay products manufacturers in The Netherlands, Ireland and the United Kingdom. Whilst half of the project costs were covered by European Union Funding the remainder has been provided by industrial sources in each of the partners countries plus Belgium.

S2.1

The project proposer and co-ordinator was British Ceramic Research Ltd (CERAM Research) and their partners in the project were the Netherlands Organisation for Applied Scientific Research TNO in the Netherlands and Forbairt in Ireland.

CERAM Research is an industrial research, development and testing centre for the Ceramic Industry carrying out projects for UK and foreign industrial companies, the UK government and is involved in the EUREKA programme. The work involves the development and

application of innovative technology in the building materials, tiles, sanitaryware, tableware, refractories and engineering ceramics areas. The annual turnover is some 8 million ECU and there is a staff of 190 persons. In the clay building materials industry it carries out work on both production technology and the products in use. It has always had, as an important part of its work, the use of energy and the heat treatment processes as applied in manufacturing. Kiln emissions have formed part of this work.

TNO is the Netherlands Organisation for Applied Scientific Research. This independent body comprises 15 specialised institutes. Its primary tasks are to support and assist trade and industry, governments and others in technology innovation and in solving problems. TNO is a fully independent R&D organisation with a staff of over 4000 and a total turnover of approx. 350 million ECU a year,. Features of TNO are: multi-disciplinary, practice - and market oriented, independent, unique know-how and facilities and international in scope.

TNO Institute of Applied Physics (TPD) is one of the 15 TNO institutes with a staff of over 380 and a turnover of 30 million ECU. TPD has a 50 year track record in contract research for industry and government. Some 2000 multi-disciplinary projects are handled each year. Applied in-house expertise in these projects comprises acoustics, optics, information technology, process physics, electronics and materials research. TPD has close ties with the technical universities of Delft and Eindhoven. Activities range from research and development to consultancy, advice, evaluation and testing.

TNO-TPD Materials Research & Technology Eindhoven is TNO's centre for materials research and technology related to inorganic materials. Expertise is concentrated on inorganic chemistry, glass, ceramics and coatings. Key issues are optimisation of production and manufacturing processes, material and product development. The department is branch-wide oriented to the glass and ceramics industry and is on the other hand the centre for development of functional and structural applications of inorganic materials, products, powders and coatings. Both process technology and materials science are covered: technology of melting, drying, sintering, forming, coating, and product manufacturing as well as synthesis of inorganic compounds, material and product development, characterisation and product testing for quality control. The department has a staff of 50 scientists, divided over 5 research groups: inorganic chemistry, traditional ceramics, technical ceramics, glass technology and glass products. The yearly turnover reaches 6 million ECU, raised from research contracts from national and international industries. The department is affiliated with the Eindhoven University of Technology, located at its campus, and has also special relations with the Delft University of Technology.

Forbairt is the Irish Government's principal non-University centre for Science and Technology and the main supplier of technological services to industry in Ireland. It has a major role in technology transfer activity. For 20 years Forbairt has had an involvement in ceramic science and technology. Its laboratories are well equipped with state-of-the-art materials characterisation instrumentation and fabrication of equipment. The joint Ceramics and Coatings Research Unit at Forbairt was established as part of the Materials Ireland programme which is a government sponsored initiative dedicated to the application of materials technology for industrial development in Ireland. It is currently a partner in several Brite-Euram projects. Forbairt will provide the chemical and mineralogical test facilities to characterise the clay raw materials from the participating industrial plants.

S2.2 Management

The 1st July 1994 was the starting date of the project and it finished on 30th June 1997. It was managed by a Steering Committee on which sat representatives of the industrial research organisation partners engaged in the work programme. It was chaired by a representative of the co-ordinator CERAM Research. This Committee met every six months, throughout the whole three year period of the research contract, to review progress and results against the planned programme and to consider modifications, if any, necessary to the programme in the light of experience gained and results obtained in carrying out the work. At these meetings detailed technical discussions were undertaken upon presentation of results by each of the partners which served to encourage co-operation and ownership of the results no matter which partner was primarily responsible for producing them. In between these meetings regular contact between the partners was maintained in writing, by telephone and fax. A list of these meetings is given at the end of the chapter.

Immediately following each Steering Committee meeting there was a meeting of the Project Advisory Group. This Group was composed of representatives from the companies and organisations providing the industrial funding for the project and the members of the Steering Committee. It was chaired again by a representative from the co-ordinator CERAM Research. At the Advisory Group meetings the Steering Committee presented a progress report outlining the main results of the work since the last meeting. In discussion views were sought from the industrial representatives as to the work being carried out and the general direction of the project as achieved and planned. Their suggestions led to changes being made to the project programme to more closely reflect their interest in the evidence revealed.

The UK industrial funding came from the Brick Development Association, a representative body of the brick manufacturers, and at their Manufacturing Executive Committee meetings CERAM Research presented a brief progress report on the project to them.

In the Netherlands the industrial funding was provided by NOVEM the national energy efficiency organisation and a consortium of Dutch heavy clay manufacturers. The additional funding in Ireland was part industrial and part from Forbairt own sources.

Regular progress reports were submitted to the European Commission DGXII every six months and in addition a mid-term review report was prepared and submitted at the end of 1995. The project was reported on at the European Workshops on Technologies for Environmental Protection in Bilbao Spain 31st January - 3rd February 1995 and also in Copenhagen at the same meeting 13-15 November 1996 by CERAM Research and TNO respectively.

TNO present a paper entitled "Mechanism of Fluoride Emission from Clay Materials" at the Pac Rim 2 International Ceramics Conference Cairns Australia 15th - 17th July 1996.

A paper entitled "Fluoride Emission from Clay Materials" was presented by TNO at Fifth E Cer S Conference of the European Ceramic Society 22-26 June 1997, Versailles, France.

TNO also wrote an article entitled "1994-1997 Three Years Investigation of Fluoride Emission Abatement" by A H deVries KGK Klei Glas en Keramiek 17 (9) September 1996.

Steering Committee Meetings :

Date	Venue
24th August 1994	Dublin, Ireland
1st December 1994	Stoke-on-Trent, U.K.
7th June 1995	Eindhoven, The Netherlands
30th November 1995	Dublin, Ireland
6th June 1996	Gatwick, U.K.
28th November 1996	Geldrop, The Netherlands
20th-22nd May 1997	Stoke-on-Trent, U.K.

CHAPTER S3

WORK PLAN PROJECTED AND ACHIEVED

The project objectives were to be achieved by the completion of five tasks each made up of a series of sub-tasks. A flow chart representing these tasks and their relation to the achievement of the four primary objectives is shown in Figure S1.

S3.1 Task A Reduction of Fluoride Emission by Process Optimisation

This was the main task of the whole project and all the partners were involved in working on this task. It was broken down into six sub-tasks.

S3.1.1 Sub-task A1 was the selection of clay types and industrial kilns. The kilns and product types were selected in all collaborating countries to cover the major clay types used for heavy clay product manufacture.

The raw material types were pre-selected for each country based upon existing knowledge of the important ones used. The ones selected in the UK were :-

Coal Measure Shale - Upper Carboniferous (Westphalian A-C)

Etruria Marl - Upper Carboniferous (Westphalian B-C)

Weald Clay - Lower Cretaceous (Hauterivian - Barremian)

Those selected in Ireland were :-

Carboniferous Shale - Upper Carboniferous (Westphalian A)

Keuper Marl - Triassic (Ladinian - Norian)

Those selected in The Netherlands were :-

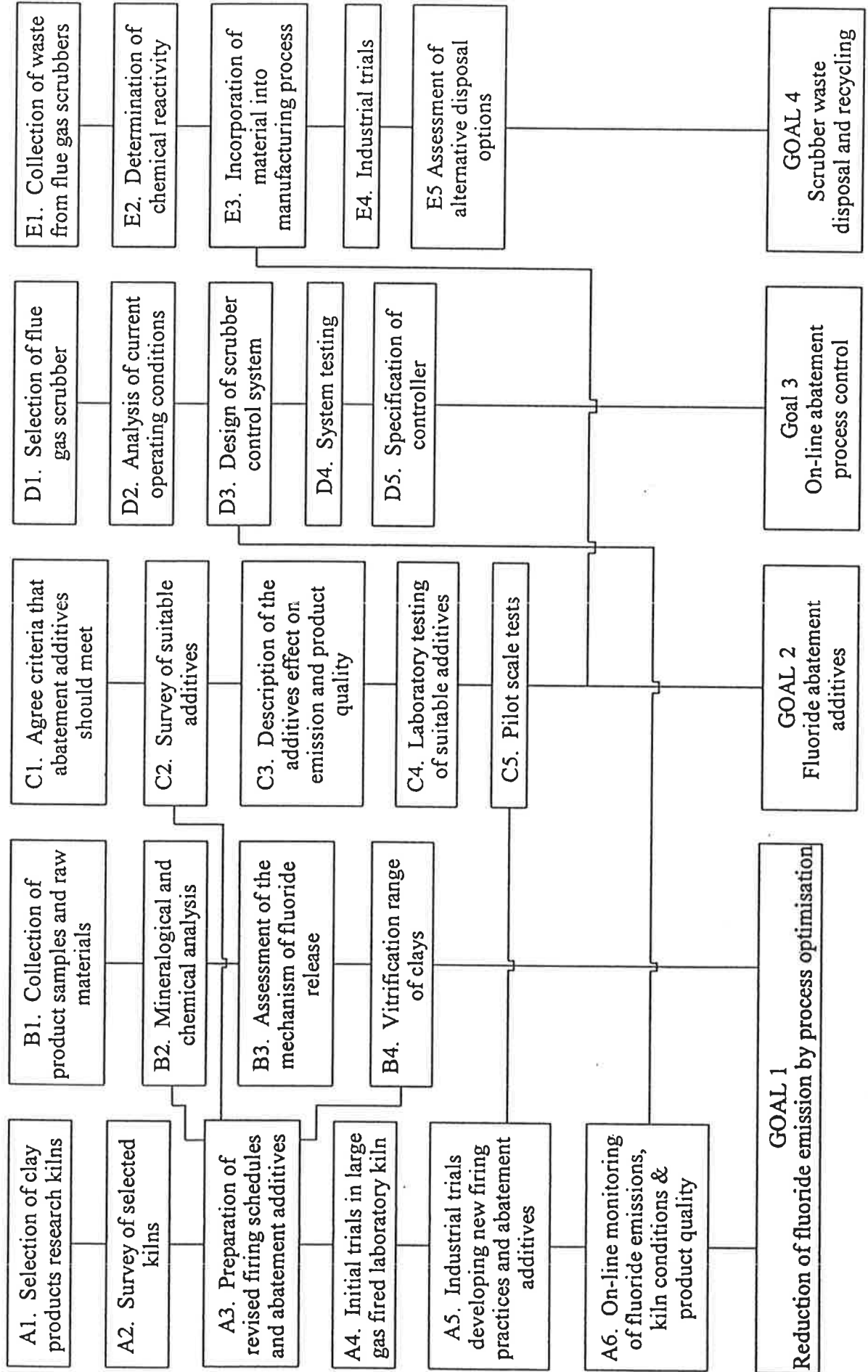
Maas clay - Alluvium (Recent)

Westerwald clay

The Westerwald clay was subsequently changed to Loess (Pleistocene) deposit, at the request of the Dutch brick industry.

Collaboration between the partners was to have been such that the broadest range of continuous types of kiln were to be chosen within the constraints of time and finance available to the project. The selection of the kilns was also to be governed by the possibilities for the adjustments to their operation to encompass the variables noted in sub-task A3. It was recognised that it would not be possible to cover all variables on any one kiln but it was intended to cover all variables between the kilns. They were selected to allow the maximum possible development opportunities for cleaner firing by process modification. Three kilns were chosen in the UK, two were chosen in Ireland and two were chosen in The Netherlands. As it happened all the kilns chosen were tunnel kilns contrary to the original intention but these kilns are by far the predominant type of continuous kiln in use in the heavy clay industry in these countries and the industry was of the opinion that this type of kiln was the only type of

Figure S1. Project Flow Diagram



continuous kiln that would be important in the foreseeable future. Subsequently individual experiments were carried out on other tunnel kilns as opportunities presented themselves.

S3.1.2 Sub-task A2 was a survey of the operating conditions of the selected kilns. The current level and variation in the level of fluoride emission from the selected kilns when firing the selected type of the product was to be established either by using factory records or contemporary monitoring records. This work was to be undertaken to establish baseline values against which values obtained subsequent to making modifications to the kiln operation could be judged.

Each kiln was to be surveyed to determine the extent to which its operational variables could be altered without affecting baseline brick quality criteria, i.e.

temperature profile
kiln atmosphere
airflow and draught control within the kiln
geometry of the setting

S.3.1.3 Sub-task A3 was the preparation of revised firing schedules and body compositions. The chosen clays from the three partners were to be examined by TNO in their unique laboratory furnace in which on-line emission measurement of fluoride is possible. The results of these tests and the information obtained in sub-tasks A2, B2 and B4 were to be used as a base for this sub-task. Three separate revised firing schedules and body preparations were to be prepared for each clay type, which could be achieved practically within the selected industrial kilns. The variables to be considered were :-

heating rate
peak temperature
peak temperature dwell periods
kiln draught
oxygen concentration in the kiln
water vapour concentration in the kiln
body composition (abatement additives)
setting geometry

This planned progression was in fact not achieved for two reasons.

- i. it was found that laboratory experimental firings in intermittent kilns do not give the same fluoride emission results as are actually found in production kilns; and
- ii. the variables to be studied in works trials are actually controlled by the kiln chosen, its operating conditions, the products being manufactured and factory output targets to be achieved.

Therefore discussions were held with the company production staff at the selected factories where the kilns were located and the parameters which could be varied were decided. The result was as anticipated that whilst all the variables listed above could not be studied on any one kiln, all variables would be examined across the range of factories co-operating in the industrial trials phase.

S3.1.4 Sub-task A4 were initial pilot trials in a large laboratory kiln of the schedules identified in sub-task A3. Batches of approximately 200 bricks were to be fired in a gas fired intermittent kiln within which the atmosphere could be controlled.

A baseline firing replicating the conditions of the host factory would be carried out with emission monitoring and product quality testing. This work was put into the programme to reduce the technical and financial risk exposure of conducting research firings in factory kilns. The schedules bringing about the largest fluoride emissions reductions whilst still maintaining product quality were to be the ones used in the next sub-task A5, the industrial trials. Pilot firings containing abatement additives would also be carried out, the resulting fluoride emission levels and product quality results then compared with the baseline data. The product quality criteria were to be fired colour, compressive strength and water absorption.

It was decided to curtail the amount of effort put into this sub-task for the first reason quoted for the deviation from the programme in sub-task A3. However, useful data on product quality was obtained from these pilot firings. The saving in time and money achieved by this curtailment was put into the next sub-task, A5.

S3.1.5 Sub-task A5 was the carrying out the industrial trials on the host factories. Initially the trials carried out were to be chosen according to the results obtained from sub-tasks A3 and A4. However, as stated above the variables to be studied are actually controlled by the kiln, its operational conditions and the type of product being manufactured. The method by which the variables were chosen were those just stated above plus the practical experience of the works management as to what was possible with their kiln. In the event opportunities arose which enabled more and different trials to be undertaken on the factories.

It was intended that the changes would be made in incremental stages to avoid catastrophes but because of the help and advice of the production staff at the factories this became unnecessary. These trials were to be carried out over a twelve month period but by curtailing some of the earlier sub-tasks it was necessary to extend this sub-task to 20 months.

S3.1.6 Sub-task A6 was the emission monitoring and product quality testing during the industrial trials carried out in the previous sub-task. This sub-task became relatively more important due to the curtailing of sub-task A4 and the expansion of A5.

Each partner was to carry out Task A requirements on the host factories in their countries according to the agreed programme and its subsequent modifications. General approach to the work and data to be collected were agreed at the outset.

S3.2 Task B Mineralogical and Chemical Analysis of the Raw Materials

This task was planned to provide basic information concerning the raw materials being used in the first objective of this project. It was to provide mineralogical and chemical data on these clays and to use that data to assess any correlations between chemical properties and physical factors and the amount of fluoride released. At the same time it was hoped to be able to understand better the mechanism of fluoride release. Forbairt had overall responsibility for this task in the programme although all partners contributed to the work undertaken. This task was divided into four sub-tasks.

S3.2.1 Sub-task B1 was the provision by each partner of representative samples of the raw materials studied in the project which had to be sent to Ireland and The Netherlands.

S3.2.2 Sub-task B2 was the mineralogical and chemical analysis of the seven selected clays. The techniques that were employed were X-ray diffraction, optical microscopy, differential thermal analysis and simultaneous thermogravimetry, X-ray fluorescence (XRF) and inductively coupled plasma (ICP). Pyrohydrolysis and ion specific electrode techniques were used to determine the fluoride content of the clays.

S3.2.3 Sub-task B3 was the assessment of the mechanism of fluoride release during the firing of the each of the chosen raw materials. Each one was monitored for the time temperature relationship with respect to fluoride emission. In addition using the results from sub-task B2 and these laboratory findings attention was focussed on a general understanding of the mechanism of fluoride release. This work was expanded with an in-depth study of the mechanism of fluorine release. This was considered an important addition to the programme in view of the ability of calcium carbonate in a raw material to capture fugitive fluorine from within the product and also from the kiln atmosphere in the preheat zone.

It was intended to try and establish whether any correlation existed between the level of fluoride emission from the kilns and the quantity and form in which the fluoride was present in the raw material. As the project progressed it became apparent that there was the factor of reabsorption in the preheat zone of the kiln and conditions in the zone above 900°C in the kiln which had far more effect on the fluoride emission than the chemical form of the fluoride and the quantity in the raw material.

S3.2.4 Sub-task B4 was to establish the vitrification characteristics of the raw materials. This was to provide information and data for sub-tasks A3, A4 and A5 when considering the possibility of investigating revised firing schedules and change to peak temperatures and peak temperature dwell times for each raw material.

S3.3 Task C Survey of Fluoride Emission Abatement Additives

This task was planned to be a combination of desk research investigation and experimental testing using the laboratory on-line fluoride measuring equipment. This was to be followed up by industrial trials by all three partners.

S3.3.1 Sub-task C1 was an agreement between all the partners of the technical and economic criteria that pollution abatement additives must meet to be effective in the heavy clay industry. This aspect of this task was completed satisfactorily.

S3.3.2 Sub-task C2 was the literature survey to determine suitable additives to the basic raw material which may assist in fluoride abatement. The approach was to include raw material vitrification modifiers to either reduce the peak firing temperature and/or the period of time that the products spend above 900°C in the firing process. It was planned that a shortlist of five potentially useful additives that could be economically utilized for pollution abatement would be produced. A list of potential additives has been produced. This sub-task was expanded to give a more detailed consideration to the chemical and physical criteria which govern the reactions of calcium carbonate as a fluoride reactive additive to a natural raw

material. This effectively dealt with the planned programme of work for sub-task C3 as far as the mechanism of how calcium carbonate behaved as a fluoride abatement additive. The remaining aspect of sub-task C3 product quality parameters was dealt with as an aspect of sub-task C5.

S3.3.3 Sub-task C4 was a laboratory investigation of the additives. As the project had progressed it became apparent that industry were very interested in the use of calcium carbonate as an abatement additive. It had also become apparent that calcium carbonate had very little effect on the emission of fluoride in intermittent kiln firing conditions and so the programme was modified to study the effect of fluoride concentration in the kiln atmosphere on the abatement efficacy of calcium carbonate.

S3.3.4 Sub-task C5 was planned that each country would produce bricks with two types of fluoride abatement additive and that these would be fired in a large laboratory kiln so that fluoride emission and product quality could be tested. Firstly because of the fact that such firings do not give realistic emission of fluoride results which one would expect in an industrial kiln because of the lack of the reabsorption process and secondly because of the industrial interest in the use of calcium carbonate the programme was changed.

It investigated the effects of different levels of calcium carbonate addition on product quality and the work was expanded to include more industrial trials not originally envisaged.

S3.4 Task D - On-line Abatement Process Control

This task was planned to utilize a continuous fluoride monitor which had been developed to control the operation of a dry limestone flue gas scrubber to enable a more efficient use of the limestone absorbent and reduce the solid waste for disposal from such a scrubber.

S3.4.1 An operational flue gas scrubber was selected and the current operating conditions were to be monitored. The fluoride content of the gases both before and after the scrubber were checked and the waste material from the scrubber was analysed. The operation of the scrubber, the amounts of discharge, the peeling frequency and the use of limestone were noted.

S3.4.2 A closed-loop control system was to be designed utilizing the output from the continuous fluoride monitor to regulate the operation of the discharge screw feeder and peeler drum. The controller was to be built and installed on the chosen operational dry limestone scrubber. The control system was set to maintain a pre-determined fluoride emission level and minimise the limestone consumption by discharging reacted material only when necessary.

S3.4.3 A pre-production specification for the control system was drafted as planned. This whole task in this project was carried out and completed as planned.

S3.5 Task E - Safe Disposal of Waste from Dry Limestone Flue-Gas Scrubbers

It was recognised that whilst dry limestone scrubbers solve one environmental problem by reducing the emission of gaseous fluoride pollutants to atmosphere, this very process creates another problem of solid waste disposal. It was therefore planned to look more closely at this solid material and at the disposal options available.

S3.5.1 Four different source dry limestone flue gas scrubber waste samples were collected and these were analysed chemically and mineralogically to determine their composition. The waste was also leached with acid, neutral and alkaline solutions and the leachate analysed to identify the species present.

S3.5.2 The extent to which the scrubber waste could be recycled into the manufacturing process in the heavy clay industry was investigated in the laboratory. It was also planned to carry out pilot firings in the large laboratory kiln but in the event, with the experience of the limitations of such firings previously experienced in sub-task A4 in this project, more emphasis was placed on factory trials. The effects of fluoride emissions were to be measured and they should provide a more realistic value than those which would have been obtained from the pilot trials in an intermittent kiln. The effect on product quality was to be checked too.

S3.5.3 Alternative disposal options for the solid waste material were to be considered for example as a chemical industry feedstock, as a filler material in plastics, etc.

S3.6 Summary

The original project plan offered to the Commission was fully carried out "with some minor changes". This has led to new knowledge of the fluoride release mechanism that takes place in the ceramic manufacturing process. With this new knowledge it is possible to get a better understanding of fluoride emission and also respond to the developing interests of the industrial partners in this field of investigation.

CHAPTER S4

RESULTS SUMMARY

S4.1 Initial Trials

S4.1.1 TNO Pilot Trials

The initial laboratory trials carried out made use of TNO controlled atmosphere tube kiln to fire clay test pieces. They produced reference samples and fixed firing conditions to compare the emissions of HF from all the clays used in this project and also the HF absorption capabilities of them too.

In addition with one of their own clays they also looked at two mixes containing 5% and 20% extra CaCO_3 than in the basic clay.

Table S4.1.1 Reference Emission and Absorption of All Selected Clays

Clay	Reference HF Emission mg kg^{-1} fired	Reference HF Absorption %	CaO Content % of Dry Clay
Coal Measure Shale	610	27	0.40
Etruria Marl	420	24	0.58
Weald Clay	270	35	2.87
Loess Rood	372	58	2.74
Loess Brons	360	59	5.15
Loess Geel	355	67	11.78
Alluvium	600	50	5.13
Keuper Marl	580	53	3.53
Carboniferous Shale	480	43	0.38

Looking at the results where the lime content had been deliberately modified because of the known absorbing properties of this chemical with regard to hydrogen fluoride it is interesting to note that the increased lime content made very little difference to the quantity of HF absorbed by these samples. In fact in general from these experiments there was no relationship between the amount of HF absorbed and the lime contents of any of them. It must be remembered that the CaO contents quoted are a total for that oxide and there is no indication of the mineral source of that lime save in the case of the Loess Brons and Geel where the additional lime was known to have been in the form of calcium carbonate. The reference HF emissions in terms of mg kg^{-1} of fired product were much higher than the levels measured on the factories. Clays with low CaO content do show absorption too, indicating an absorption mechanism other than reaction with lime.

The good atmosphere control obtainable in this kiln allowed a series of experiments to be undertaken to determine the effects of other factors like kiln atmosphere, moisture content, flue gas flow rate, heating rate, sample geometry and peak temperature which are known to affect HF emissions. These tests were carried out on the Loess Brons clay.

Hydrogen fluoride emission is very low in dry air but when only a very small amount of moisture is present, there is a large increase in the mass of HF emitted but if the water vapour content is increased to 15% the increase in HF emitted is not proportional.

Table S4.1.2 Effect of Water Vapour on HF emission

H ₂ O %	HF emitted mg kg ⁻¹ fired
0.0	20
1.2	175
15.0	300

This behaviour had also been noted with other clays not included in this project. Unfortunately the ability to control water vapour content in an industrial continuous kiln does not usually exist and so the practical value of this finding is of no use to existing kilns.

Increased gas flow increases the HF mass emission but the influence is not so marked as in the case of water vapour but again the increases are not proportional.

Table S4.1.3 Effect of Gas Flow on HF Emission

Flow l min ⁻¹	HF Emission mg kg ⁻¹ fired
4.5	175
10.0	240
21.0	280

The influence of heating rate confirmed the observation made in the intermittent kiln at CERAM with the British clays. The faster the heating rate the lower the HF emission. These experiments also clearly showed that this emission is a function of increased temperature and particularly the time spent between 900 and 1100°C.

Sample geometry tests compared uniform dimension pieces in two directions with a variation in the third, thickness. This showed that slightly higher emissions of HF by mass occurred with the thinner pieces. This is a surface area to volume ratio factor affecting the permeability of gases in and out of the pieces. The effect of this will be seen in the industrial experiments. The variation in emission quantities of HF is not constant for all raw materials with equivalent surface area to volume differences.

The experiments to study the influence of peak temperature on HF emission were different from the previous ones reported in so far that besides the standard clay, the same clay with over twice the lime content was used too. As expected the initial emission rate increases with temperature, the higher the temperature the higher the emission rate, but there is a decrease during the dwell period at the higher temperatures. This could be due to either or both of two causes :-

- (i) reduction in the amount of fluoride available.
- (ii) sintering leading to the encapsulation of the fluoride containing phases.

The HF emission curves are almost identical for both these samples although one contains over twice the lime content of the other which seems to suggest that this has not got much influence on HF emission. However, this is known not to be the case and the apparent contradiction will be explained under task B in this summary report.

S4.1.2 CERAM Research Pilot Trials

All these trials were carried out in a large laboratory intermittent kiln, natural gas the fuel.

S4.1.2.1 Factory UK1

Faster car push rate and faster car push rate with higher peak temperature together with the factory schedule were all simulated. Both the changes shortened the time interval over which the hydrogen fluoride is evolved and resulted in a reduction in the total mass of HF emitted, and also in the mass emitted per kilogram of fired brick. The total fluoride emission by mass was reduced by 30% by the faster car push rate and by a further 5% when the peak temperature was increased.

Table S4.1.4 Initial Laboratory Trials UK1 Factory

Schedule	Total Emission g	Mass Discharge gkg ⁻¹ fired brick
Factory	211.1	0.54
Faster Push	147.2	0.38
Faster Push plus Higher Peak Temperature	134.7	0.35

There was a small increase in the peak HF emission concentration of about 4% for both alternative schedules. The quality of the fired bricks produced were all within the manufacturers specification.

Table S4.1.5 Product Quality UK1 Factory

Schedule	Water Absorption 5h boil %	Compressive Strength Nmm ⁻²
Factory	5.5	76.0
Faster Push	5.9	72.0
Faster Push Higher Peak Temperature	5.0	75.9

S4.1.2.2 Factory UK2

Four alternative firing schedules were simulated using bricks from this factory. They were faster car push rate, slower car push rate, lower peak temperature and lower peak temperature with lower oxygen concentration. The normal push interval was 55 minutes, the faster one was 40 minutes, the slower one 70 minutes, normal peak temperature 1150°C the lower 1050°C, normal oxygen level 10.8% lower 5.5%.

In these trials the faster car push rate resulted in an 11% decrease in the total HF emitted by mass but a 25% increase in the peak HF concentration. The rate at which HF was evolved was also greater than when the factory schedule was used. The simulated slower push rate resulted in no measurable change in the total HF emitted by mass but the peak HF emission concentration was reduced by 9%.

A lower peak firing temperature resulted in a reduction in the peak HF concentration emitted but there was an approximate 10% increase by mass in the total HF emitted with a slight increase by mass in HF emitted per kilogram of fired brick.

The final trial firing simulated the factory schedule but with the lower peak temperature and for part of the time a reduced oxygen concentration in the exhaust gases. When comparing the reduced oxygen with the normal oxygen level periods of the firing, the former produced a 44% reduction in the total mass of HF emitted but a 39% increase in the peak emission concentration. Here the overriding factor is the reduction of mass flow through the kiln. The lower oxygen content was achieved by reducing the air input through the burners. This had the effect of increasing the HF concentration in the kiln atmosphere so suppressing its emission from the bricks.

All the bricks produced by firing to the factory temperature of 1150°C were within specification (5 - 6% water absorption 5h boil, 60-70 Nmm⁻² compressive strength) but those fired to the lower temperature, 1050°C, were below specification with double the water absorption value and half the compressive strength value. Therefore whilst the large reductions in HF emitted by mass were achieved they were done so at the expense of quality which renders such reductions unobtainable in practice.

S4.1.2.3 Factory UK3

The effects of faster push rate and higher peak temperature were investigated in these initial trials. The normal push interval time is 57 minutes and this was reduced to 40 minutes and the peak temperature was increased from 975°C to 1000°C.

This factory has much lower emission levels of HF by mass than the other two factories. But in common with the trends already observed in the previous initial trial firings the total HF by mass emitted is reduced, in this case by 10%, and the peak concentration increased when the heating rate is increased. But if the peak temperature is increased the peak concentration of HF increases too and the mass emitted increases by some 6%.

The HF concentration curves obtained on the trials with bricks from this factory showed a feature not seen on the others and this was a sharp rise in the emitted HF at the beginning of the cooling schedule even though the flow through the exhaust remains more or less constant. A probable explanation for this phenomenon may be that when cooling begins, more air and hence more oxygen enters the kiln through the burners since there is no gas being burnt to use some of the oxygen. This increase in kiln atmosphere oxygen level encourages the coke breeze fuel in the bricks to burn which in turn results in a temporary temperature rise within the bricks and a burst of HF is released but as the temperature falls this quickly dies away. The coke breeze in the unfired bricks is a practise peculiar to this UK factory in this project. The quality of all the bricks produced in these trial firings were within the manufacturers specification.

S4.1.2.4 Summary

A reduction in time above 900°C by firing to a faster schedule causes a reduction in the total mass of HF emitted but an increase in the peak concentration measured. An increase in peak temperature will also cause an increase in peak HF concentration.

Table S4.1.6 HF Emission Data

Clay	Reduction in Time above 900°C %	Reduction in Total mass HF emitted %	Increase in peak HF concentration %
Coal Measure Shale	33	30	4.5
Etruria Marl	27	11	25
Weald Clay	29	10	35

Table S4.1.7 HF Emission Data

Clay	Increase in Peak Temperature %	Increase in Peak HF Concentration %
Coal Measure Shale	2.4	8.8
Etruria Marl	9.5	63.2
Weald Clay	2.6	40.4

The reduction of oxygen concentration by 50% reduces the total mass of HF emission by some 44% but it is considered that the actual suppression of its emission is caused by an increased concentration of the HF in the kiln atmosphere.

The data from this series of pilot scale firings has provided some useful insights into the HF emission process and the likely changes in product quality if certain firing schedule changes are made. However, they were carried out in an intermittent kiln and therefore there is no possibility of the absorption process which takes place in the pre-heat section of a continuous kiln firing having any effect. This fact therefore prevents the direct transfer of the expected magnitude of the changes measured to the continuous kiln situation.

S4.2 Industrial Trials and Emissions Monitoring

All the partners in this project have undertaken trials in their own countries on industrial tunnel kilns. Initially three such kilns were chosen in the UK, two in The Netherlands and two in Ireland but as the project progressed opportunities arose to use additional tunnel kilns in each country. None of the additional kilns were surveyed as were the original choices but they were all used for either only one experiment or only on a comparative series of experiments where the lack of initial survey information was not regarded as in any way prejudicial to the results obtained or the project as a whole. All the kilns used for these trials used gaseous fuel except one which used a mixture of gaseous and liquid fuel.

The variables affecting fluoride emissions investigated on the industrial kilns were :-

- firing schedule
- peak temperature
- time above 900°C
- kiln draught and atmosphere
- reabsorption and preheat conditions
- setting geometry
- abatement additives
- surface area to volume of setting

S4.2.1 Kiln Schedule and Peak Temperature

The firing schedule for a product is set by the temperature profile along the length of the tunnel kiln and the car push time interval. Keeping the preset kiln zone temperature the same

it is easy to alter the schedule within limits by changing the car push interval time. This change was carried out on factories UK1 and UK2.

S4.2.1.1 UK Factory Trials

The trial carried out on UK1 factory investigated three half car push intervals, 30, 36 and 42 minutes, the 36 minutes interval was the normal one for the kiln temperature profile used.

When the firing schedule was shortened by reducing the push interval time from 36 to 30 minutes, the mass of fluoride emitted per unit time increased from 2.46 to 2.99 kg h⁻¹ and the mass discharged per brick increased slightly from 0.32 gkg⁻¹ to 0.33 gkg⁻¹. The HF concentration also increased from 94 to 109 mg m⁻³. The increase in concentration had been noted in the intermittent kiln firings of these bricks, but the increase in mass of fluoride discharge was the opposite of what had been observed in the laboratory although the mass discharge per kilogram of fired brick was slightly down on the result obtained in the intermittent kiln firing. This last result is explained by the fact that reabsorption of fluoride is taking place in the tunnel kiln and this does not happen in an intermittent kiln. The faster firing schedule means that the bricks not only pass faster through the high temperature HF emission zone but also through the HF absorption zone in the pre-heat section of the kiln so reducing the time for this reabsorption to take place. Also part way through the faster schedule trial the maximum kiln temperature was raised to maintain the quality of the product and it is known that this will increase the discharge of fluoride from a clay. This temperature rise together with the reduced reabsorption time more than counter balanced the reduced mass emission which would be expected from a 17% shorter time above 900°C.

When the firing schedule was slowed by extending the half car push interval to 42 minutes the HF concentration decreased below the 30 minute interval level but was still above the 36 minute level, but the mass of HF discharged increased too although the peak temperature was reduced and the absorption time extended. In this case it is the time above 900°C that is the dominant factor affecting the fluoride emission. Tests carried out at TNO have shown that the raw material used at this factory has next to the lowest reabsorption capacity of all the materials studied in this project and therefore the comparatively insignificant influence of reabsorption with this material is in accordance with their findings. This material also had the highest fluoride emission in the laboratory of all the clays in this project at 610mgkg⁻¹ fired weight.

It can be seen that the 36 minute half car push interval is the optimum one to minimise fluoride emission for this raw material fired in this kiln.

The parameters of firing schedule and peak temperature dwell time were studied at UK2 factory. Once again the schedule was altered by changing the full car push time interval and keeping the set temperatures in the zones of the kiln constant. Two time intervals were used 75 and 60 minutes for 2 and 3 days duration respectively. During the third day of the 60 minute push interval the set temperature in zone 5 of the kiln was reduced 50°C this effectively halved the time spent at the top temperature of 1150°C. However, after 12 hours this change had to be reversed because of the destabilizing effect it had on adjacent zones of the kiln.

The reduction of the time above 900°C increased the HF concentration by 2.6% which was an order of magnitude less than the increase observed in the initial intermittent kiln firings. However, any comparisons between these two sets of results for this particular raw material must be tentative since besides the fact that the same push time intervals were not used in the calculation of the intermittent kiln firings schedules, no reabsorption was taking place in these either but it is in the factory kiln.

Decreasing the peak temperature dwell period decreased the mass flow of HF by 8.2% but the reabsorption conditions were not affected in so far as this comparison has been made with the same push interval time. It therefore seems in this kiln with this material and at the comparatively high peak temperature, it is the peak temperature dwell that has the greatest influence on fluoride emission.

S4.2.2 Limestone Addition to the Raw Material

The addition of limestone to a clay mix is a known method of reducing fluoride emissions when firing clay. It was appropriate also to study this process since there is interest within the heavy clay industry and some manufacturers already add limestone to enable them to produce cream and yellow coloured bricks from a red burning clay. This is the case in The Netherlands.

S4.2.2.1 Industrial Trials Factory NL1

This factory produce bricks which require two levels of calcium carbonate addition to their loess clay which contains 2.74% by mass CaO. The two addition levels are 5% and 20% by mass calcium carbonate.

In general there was a distinct cyclic pattern to the fluoride emissions and oxygen levels in the exhaust gases. Each push of the cars the oxygen level increases rapidly from 17.5% to 20.5% as the burners are turned off. The addition of 15% extra CaCO₃ by mass lowers the fully corrected fluoride emission concentration from 7.6 to 2.9 mgm⁻³ at STP dry and 18% O₂, this is a reduction of 62%.

Such large additions of calcium carbonate necessary to bring about dramatic reductions in fluoride emissions would be unacceptable to many brick manufacturers because of the effects on fired colour and product properties. Some laboratory experiments to address the former problem of colour by iron oxide additions are described in the section of the report covering task C additions.

S4.2.2.2 Industrial Trials Factory NL5

At the factory an addition of 10% calcium carbonate was added to a red burning clay and as a result the colour changed to yellow but the HF concentration in the exhaust gases was reduced from 15 mgm⁻³ to 3.7 mgm⁻³ at STP and 18% O₂. This reduction was again brought about by the reabsorption of fluoride by the limestone in the bricks.

S4.2.3 Effect of Oxidation and Reducing Conditions in the Kiln on Fluoride Emissions

Research work undertaken in the laboratory at CERAM Research in 1992-93 had indicated that firing clays in an oxygen deficient atmosphere reduced fluoride emission. These experiments had been carried out under continuous reducing conditions. Other than for the firing of blue bricks reduction periods are normally of comparatively short duration and it was decided to see what effect such conditions had on fluoride emissions.

S4.2.3.1 Industrial Trials

Factory trials in the U.K., Ireland and Netherlands were undertaken in kilns where reducing conditions are induced for brief periods in each kiln car push cycle. The percentage of the cycle time when reducing conditions were induced in the firing zone varied between 15 and 30% of that time. In none of these trials did this change have any affect on the emission of fluoride.

S4.2.4 Setting Geometry

Since reabsorption of fluoride in the preheat zone of a tunnel kiln can have a marked effect on the fluoride emission level, it was considered that if one could present an as large as possible surface area of product to the kiln gases the reabsorption process could be enhanced and the HF emissions thereby reduced. Industrial trials were designed to test this idea.

S4.2.4.1 Industrial Trial Factory NL1

The new planned setting pattern was designed to maximise the absorbing surface area of the bricks and minimise the obstruction to kiln gases flowing through it. The new setting density was only slightly less than the traditional Hulo pattern. The new setting had to be built by hand and the Hulo setting was machine formed. This imposed time constraints on the amount of new pattern that could be set, which was restricted to only part of a car setting.

Unfortunately, the results from this trial were inconclusive. The open setting encouraged the emission of fluoride in the firing zone without apparently increasing the reabsorption in the preheat zone. The residual fluoride contents of the fired bricks from the open setting were between 11 and 53% lower than the fluoride content of a brick from the dense setting. The hoped for better penetration of the setting by the kiln gases does not appear to have taken place and this is considered to have been due to the effect of the denser setting on the same car and the adjacent car. There was not an opportunity to repeat the trial with several consecutive cars of open setting to prove or disprove the idea.

S4.2.4.2 Industrial Trial Factory UK1

An attempt at investigating the effect of setting geometry was approached in a different way at this factory where the opportunity was taken to look at the effect on fluoride emission of firing cars of 80mm and 65mm thick bricks. There are 3456, 65mm bricks on a car and 2688, 80mm ones.

When the kiln was full of 65mm bricks the mass fluoride emission from the chimney was 1.6-1.7 kg h^{-1} . As the quantity of 80mm bricks increased in the preheat zone the stack emission increased to 2.0 kg h^{-1} . When the 80mm bricks were in the firing zone 65mm ones were in the preheat zone and the fluoride emission fell to 1.2 kg h^{-1} .

It was not possible to determine the equilibrium mass discharge of HF for the 80mm bricks since the kiln is never completely full with them.

S4.2.4.3 Industrial Trial Factory UK1

The effect of surface area on level of fluoride emission was seen when smooth and rustic faced bricks of the same thickness were passing through the kiln at the same time.

When there were smooth bricks in the preheat and firing zones the measured HF emission concentration was 91.2 mg m^{-3} corrected to STP and 18% O_2 . When the rustic brick was in the preheat zone and the smooth brick in the firing zone the measured HF emission concentration fell to 62.0 mg m^{-3} at STP and 18% O_2 . When the rustic face brick was in both the preheat and firing zones the measured fluoride emission concentration corrected to STP and 18% O_2 increased to 109.4 mg m^{-3} .

The rustic texturing provides the brick with a larger more open surface area so that in the preheat zone it can more readily absorb fluoride but in the firing zone it can also more readily emit fluoride. These figures indicate that the increased emission exceeds the increased absorption when there are rustic face bricks in preheat and firing zones. It must also be remembered that the raw material used at this works had next to the lowest reabsorption capacity.

An alteration in setting geometry and a larger perforation hole size at IRL1 factory on Kiln 2 resulted in a larger surface area but lower mass of material available for reaction with fluoride containing gases in the preheat section of the kiln and a larger emitting surface in the firing zone of the kiln. In this case there was a reduction of just over 53% in the mass of fluoride emitted from the kiln indicating that the reabsorption of fluoride is dominant over emission and is also an indicator that in this situation setting patterns with larger surface areas can give rise to real reductions in fluoride emissions from the kiln.

S4.2.5 Hydrogen Fluoride Concentration Profile in a Kiln and Kiln Draught

When carrying out the industrial trials on reabsorption of fluoride by bricks containing limestone TNO produced a profile of HF concentration along the tunnel kiln to indicate qualitatively and quantitatively where the fluoride was being reabsorbed. A similar exercise was undertaken by CERAM Research but in this instance the bricks did not contain added limestone. These trials validate the fluoride profile predicted from the fluoride release mechanism.

By sampling along the length of the kiln for fluoride concentration it was possible to show that the highest concentration was found where the temperature was 990°C, 332 mg m^{-3} corrected and this decreased to 124 mg m^{-3} at 500°C. By using the measured concentration of fluoride values and the flue gas flow down the kiln, the mass flow of fluoride can be calculated. The

huge reduction in the mass flow (from 6200 to 214gh⁻¹) is due to re-absorption in the pre-heating bricks. In this kiln it was calculated that the net loss of fluoride expressed as hydrogen fluoride was only some 26 mgkg⁻¹ of fired product compared to an initial increase of more than 700mgkg⁻¹.

S4.2.5.1 Industrial Trial Factory UK1

Hydrogen fluoride sampling was carried out along the length of the firing zone in the kiln through burner ports in the roof. The maximum HF concentration was measured in the zone where the temperature was 800-900°C, and the corrected value was 565.8 mgm⁻³. In the preheat zone this had reduced to 119.7 mgm⁻³, a 79% reduction. At the chimney the HF concentration corrected was down to 35.3 mgm⁻³, a further 86% reduction between the preheat measurement point and here. However, the measured gas flows down the kiln indicated a 28% increase in flow between the preheat and chimney points indicating gas flow from any preheat injection burners and in-leakage. Inevitably the fluoride concentration should decrease because of the additional gas volume measured but this would not account for the size of the decrease observed. This is an indication that reabsorption of fluoride is taking place throughout the whole of the preheat zone in this kiln.

It has been shown in laboratory trials that if one increases the fluoride concentration in the kiln atmosphere in the firing zone one can suppress the emission of fluoride. One of the few ways of trying to achieve this in a tunnel kiln, other than by fluoride injection, is to reduce the draught. A trial was carried out to monitor the effect of reducing the fan speed by 20%. This reduced the airflow by 12% and the stack HF concentration corrected by 4% but the HF mass flow was reduced by 16%.

By reducing the gas flow through the kiln in this way one also increases the time of contact between preheating products and the kiln gases which will encourage reabsorption and thereby tend to reduce fluoride emissions concentration. No measurements were taken to indicate which process, increasing the HF concentration in the firing zone or increased reabsorption, was the most important in this case.

S4.2.6 Reabsorption of Fluoride

It has already been indicated in this report that reabsorption of fluoride is an effective technique for reducing fluoride emission especially when enhanced by limestone additions to the raw material. However, other trials have been undertaken which indicate that reabsorption could be enhanced without adding limestone.

S4.2.6.1 Industrial Trial Factory IRL1

For reasons other than just to reduce fluoride emissions four extra side burners were fitted into the preheat section of the kiln. By doing this the average value of fluoride emission concentration at the stack fell from 20 to 7.5 mgm⁻³. Gas flow values were not obtained so no assessment can be made of the diluting affect of the combustion products from these burners which would cause a reduced fluoride concentration in any case. But this evidence together with the following trial results suggests that by prolonging contact between kiln gases and preheating products must increase the amount of reabsorption of fluoride. A similar alteration

was made to Kiln 2 on this factory and this resulted in a fall in fluoride emission concentration from 97 to 46 mgm^{-3} .

S4.2.6.2 Industrial Trial Factory NL3

The kiln at this factory had a separate preheater, which would be more accurately described as a post dryer or final high temperature dryer. Some of the exhaust gases from the kiln are fed into this preheater and the remainder pass straight to the stack. Measurements were made of gas flow, oxygen, carbon dioxide, water vapour, temperature together with fluoride emission concentrations at three different positions and gas flows and fluoride emissions concentration were measured at the stack too. The three positions were gases from the kiln, out of the preheater and those passing direct to the stack from the kiln.

These measurements indicated that 55% of the volume of gases from the kiln were fed to the preheater, the remainder to the stack. The fluoride concentration in these gases corrected was 63 mgm^{-3} . On leaving the preheater the corrected fluoride concentration was 2.9 mgm^{-3} . In mass terms the passage of 55% of the exhaust gases through the preheater reduced the fluoride emitted by 52%. The other significant measurement was that the flue gas temperature into the preheater was 193°C and out of it was 56°C, in other words the gases entered above the acid dew point and came out below it.

This last fact effectively makes the preheater a partially wet scrubber and this is why it is so efficient reducing, the fluoride concentration by 95%. The presence of water will dramatically increase the absorption of fluoride and it will also be removing sulphur oxide gases too although measurements were not made which would show this. The drawback to this very efficient exhaust gas scrubbing technique is of course the acid condensation that occurs on cold surfaces, be they product or preheater structure and equipment. On the former it could give rise to scumming and on the latter to corrosion. Design detailing and choice of materials could help overcome the corrosion problems.

A similar small scale trial on factory UK1 showed similar very efficient scrubbing could be achieved in a dryer.

S4.3 Mineralogical and Chemical Analyses of Raw Materials Used in this Project

This was part of Task B in the project and the aim was to determine basic chemical and mineralogical data concerning the raw materials. It was also thought necessary as background data for the study of the mechanism of fluoride release and the vitrification characteristics of these materials which also formed part of task B.

All the sub tasks were completed as laid out in the programme although the measurement of fluoride content of the raw materials did identify the need to develop a definitive test method for measuring fluoride content.

The basic mineralogical and chemical analysis was undertaken by Forbairt using a number of different relevant techniques. These were X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma (ICP), atomic absorption spectroscopy (AAS), thermal analysis (simultaneous thermogravimetry TG) and differential thermal analysis (DTA), particle

size analysis, surface area analysis and optical microscopy. Fluoride content determinations were carried out using a pyrohydrolysis technique with ion specific electrode measurement of the resulting liquid.

S4.3.1 Mineralogical Analyses

The XRD analysis of the samples was first run as powders in the cavity mounts and then, using the clay fraction ($<2\mu\text{m}$), as oriented mounts on glass slides in order to reveal further information regarding the nature of the clay minerals present. The results are given in the tables below.

Table S4.3.1 X-ray Diffraction Results (non clay)

Raw Material	Constituents		
	Major	Minor	Trace
Keuper Marl	Quartz	Calcite Plagioclase Feldspar	Alkali Feldspar Haematite
Carboniferous Shale	Quartz		Feldspar
Alluvium	Quartz	Calcite Plagioclase Feldspar	Alkali Feldspar Dolomite
Loess	Quartz	Calcite, Plagioclase and Alkali Feldspar	
Coal Measure Shale	Quartz	Plagioclase Feldspar	
Etruria Marl	Quartz		Calcite
Weald Clay	Quartz	Calcite	Feldspar

Table S4.3.2 X-ray Diffraction Results (Clay)

Raw Material	Constituents		
	Major	Minor	Trace
Keuper Marl	Illite Mica	Chlorite	Other clay minerals
Carboniferous Shale	Illite Mica Chlorite		Other clay minerals
Alluvium	Illite Mica	Kaolinite Chlorite	Other clay minerals
Loess	Illite Mica Chlorite	Kaolinite	Other clay minerals
Coal Measure Shale	Illite Mica Kaolinite	Chlorite	Other clay minerals
Etruria Marl	Kaolinite Illite Mica		Other clay minerals
Weald Clay	Illite Mica Kaolinite		Chlorite Other clay minerals

In both tables S4.3.1 and S4.3.2 the minerals are noted in any one column in descending order of importance.

The DTA revealed similar features for all these materials as far as endothermic peaks were concerned, dehydroxylation of the clay mineral and the quartz change β to α . The Coal Measure Shale, Carboniferous Shale and Weald Clay also showed exothermic peaks due to the combustion of naturally occurring carbonaceous material in the case of the first two and this plus deliberately added carbonaceous material (coke breeze) in the case of the last one.

S4.3.2 Chemical Analyses

The XRF chemical analysis results are here summarised and grouped in one table S4.3.3.

Table S4.3.3 Condensed XRF Analyses

Oxides	Keuper Marl	Carboniferous Shale	Alluvium	Loess	Coal Measure Shale	Etruria Marl	Weald Clay
Silica SiO ₂	63.4	55.4	68.4	76.5	63.9	62.8	61.1
Alumina Al ₂ O ₃	15.0	22.4	10.3	7.0	17.0	16.6	14.7
Iron Oxide Fe ₂ O ₃	5.1	8.0	4.1	2.0	6.1	8.5	5.4
Alkali Earth Oxides	5.4	2.8	7.1	6.3	1.9	1.6	3.8
Alkali Oxides	4.9	4.1	3.5	2.5	3.7	2.0	2.6
Loss on Ignition	6.1	7.2	6.4	5.8	6.8	7.2	10.2

The loess and alluvium have high lime contents which boosts the alkali earth amounts since lime is usually the major constituent of these. The loess also has the highest silica content which is probably indicative of a high quartz content. These two materials would also be expected to have the lowest clay mineral content from their alumina content with the Carboniferous Shale having the highest. All the others would be expected to have similar amounts to clay mineral. The high ignition loss for the Weald clay is a reflection of the fuel added to the clay.

S4.3.3 Fluoride Content Determinations

The fluoride content was determined by pyrohydrolysis at 850°C and the resulting distillate tested using an ion specific electrode. These results are given in Table S4.3.4.

Table S4.3.4 Fluoride Analysis Values

Raw Material	Fluoride Content mgkg ⁻¹
Keuper Marl	516
Carboniferous Shale	371
Alluvium	359
Loess	438
Coal Measure Shale	328
Etruria Marl	329
Weald Clay	564

During the project experimental work evidence came to light that the method of fluorine determination used did not necessarily give the total content of the element in that sample. Another technique using fusion gives different and somewhat higher values. The determination of a definitive method was not explored as it was considered not to be within the remit of this project, however it does need to be addressed.

S4.3.4 Vitrification Characteristics of the Raw Materials

The vitrification behaviour of each of the materials was determined by the technique of firing a small setting of six test pieces at a heating rate of 1°C per minute whilst the setting had a vertical load applied to it of 34kNm², which is approximately equivalent to the load at the base of a brick setting in a kiln. As the setting is heated a continuous plot of the change in linear height of that setting against temperature is made and after the firing reaches 1150-1200°C or the setting shrinks 10%, whichever is the sooner the test is terminated, the plot values are corrected and replotted and the resulting curve is assessed.

The initial reaction of the setting is to expand, normal thermal expansion on heating, which usually reaches a maximum of 2% linear at about 850°C.

Above this temperature the setting starts to shrink with the onset of vitrification, slowly at first but then at an increasing rate with the rise in temperature. The shape and steepness of the curves once shrinkage is taking place provides evidence of the safe maximum firing temperature and the possible range of temperature over which the clay can be fired to make an acceptable quality product. In practice the product quality has to be checked on actual bricks fired and tested subsequently.

The Keuper Marl starts to shrink above 800°C but the shrinkage ceases at about 925°C before commencing again at 1000°C. The shrinkage above 1000°C occurs at an ever increasing rate becoming rapid above 1050°C. The early period of shrinkage is due to the alkali fluxes with the pause before the alkali earth fluxes start to cause shrinkage above 1000-1050°C. Then typically with this material the shrinkage becomes rapid.

The Carboniferous Shale starts to shrink at about 850°C with a steady rate over the range 900-1075°C, above this temperature there is some evidence of slight bloating.

The Alluvium starts to shrink at 800°C but the shrinkage ceases at 900°C. This is a reflection of the low alkali content. At about 1050°C shrinkage recommences and is fairly rapid becoming rapid above 1075°C. This is the effect of the high alkali earth content.

The Loess starts to shrink at about 850°C and then pauses after 950°C until 1100°C when a rapid shrinkage commences becoming almost instantaneous melting above 1150°C.

The Coal Measure Shale starts to shrink at 850°C and then shrinks at an ever increasing rate to 1100°C and above this temperature there is some evidence of bloating. Whilst this curve is very similar to that for Carboniferous Shale the actual shrinkage at the higher temperatures is somewhat greater.

The Etruria Marl starts to shrink at 850°C like most of the other materials but the shrinkage is very slow to 950°C this is reflection of its low alkali content. Above 950°C the shrinkage increases but still remains at a constant rate up to in excess of 1150°C. This is a reflection of the very low alkali earth content. This material has the broadest vitrification range of all those studied in this project.

The Weald clay starts to shrink at 800°C although it is low in alkali. The shrinkage is then reasonably steady up to 1100°C when the rate increases markedly, this is due to the alkali earth minerals.

A study of these curves gives an indication of the scope for varying the maximum firing temperature and peak temperature dwell time for each of these materials. The Etruria Marl has greatest scope for alteration if one considers only these curves and the loess and alluvium have no scope for change upward in temperature or longer dwell at peak temperature. The information from these curves was useful in helping partially to decide the process variables that could be changed at each factory co-operating in the industrial trials.

S4.4 Mechanism of Fluoride Release

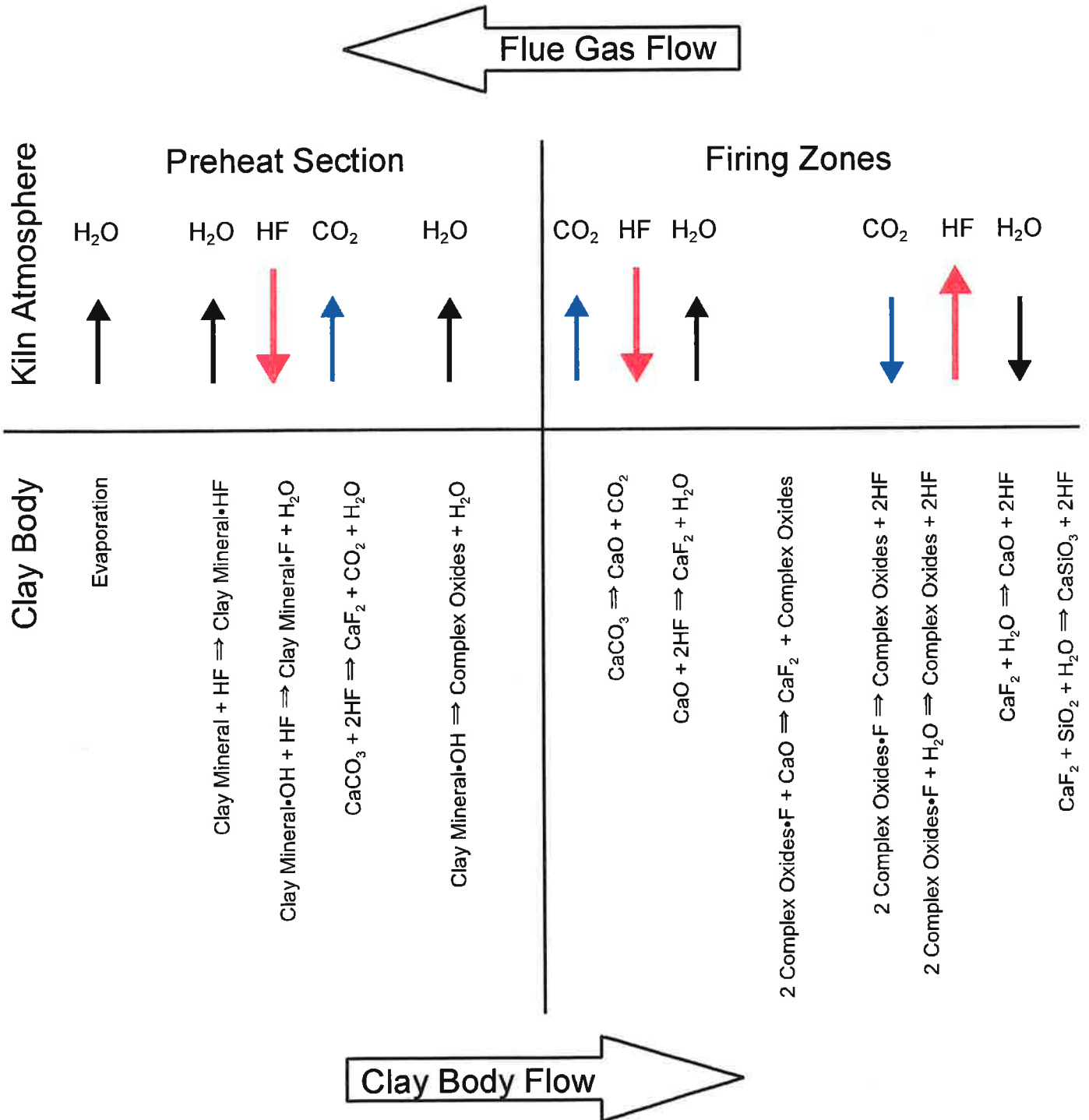
An attempt to show schematically the fluoride emission and reabsorption process can be seen in Figure S.4.4.1. The preheat and firing zones of the kiln are represented and without being specific the lowest temperatures occur on the left hand and the highest on the right hand side. The arrows indicate the passage of gases in or out of the clay body at the different positions in the kiln and beneath the horizontal line the general reactions taking place are given which are either generating the gases or causing their absorption.

S4.4.1 Fluorine into Clay Mineral

The following is a brief explanation of how fluorine can get into the clay mineral lattice.

Fluorine is found in many clay minerals and the raw materials studies in this project had fluorine contents between 328 to 564 mgkg⁻¹. The alumino silicate layers in a clay mineral have abundant electron acceptor sites on their surfaces which readily accept anions like HO⁻

Figure S4.4.1 Schematic Representation of the Fluoride Emission Process



The temperatures at which these reactions occur depends on the clay type, the processing parameters employed by the manufacturing site and the conditions prevailing in the particular kiln. Many of the reactions overlap and there may be competing reactions or processes occurring.

and F^- . These ions both have similar ionic radii (1.13-1.36 Å for F^- and 1.53 Å for HO^-) charge and polarisability which will fit into the crystal lattices of the clay minerals. The electron affinity of the fluoride ion, F^- , is 3.399 eV whilst that of the hydroxyl ion HO^- , is 1.828 eV. The stronger electron affinity of the fluoride ion is reflected in the fact that, as has been found in this project, it takes higher temperatures to drive off the fluoride than the hydroxyl ion from the clay minerals.

Laboratory experiments by other workers have shown that in a solution fluoride ions can be taken up by hydroxylic silicate and there is reasonable agreement between the mole equivalent of HO^- released and the mole equivalent of F^- absorbed, suggesting that the substitution of HO^- by F^- is stoichiometric. Infra-red spectroscopy, which provides a means of detecting actual changes in HO^- concentration, when applied to reacted layered silicate structures were also in agreement with the chemical results. This agreement in results between different analytical methods strongly supports the hypothesis of stoichiometric replacement of HO^- by F^- although none prove it beyond doubt.

There is also evidence that solutions of fluorides will "decompose" clay minerals resulting in the formation of various complex solid fluoride phases and the release of HO^- ions into solution. However, reports of the experiments indicated that decomposition of the clay mineral by fluoride solutions accounted for only part of the reaction taking place and did not account for all the HO^- ions released. Was stoichiometric replacement of HO^- by F^- ions taking place as well?

Whilst no positive evidence has been found in the literature for this stoichiometric replacement it appears to be the dominant reaction. Most layer silicate clays in the solid phase are capable of absorbing fluoride ions from solution, this accounting for the fluorine content of them.

These reactions could quite easily take place during and subsequent to the deposition of sedimentary rocks in aqueous environments and hence are appropriate reactions to consider since most of the raw materials used in heavy clay product manufacture are sedimentary rocks or derivatives thereof.

S4.4.2 Fluorine Release

The next aspect is to understand how it is released during the heat treatment processing undertaken when making the products.

Previous studies reported in the literature found that there was no direct relationship between dehydroxylation and fluoride release and that with different clay minerals the emission of fluoride in dry atmosphere firing occurs in similar temperature regions. This has been found in this project too. Previously reported work suggested that thermodynamic stabilities of F^- bonds are similar in different clay minerals. This is in agreement with the findings of this project too where it has been found that the temperature at which the fluorine is emitted is almost the same for all clays.

It is also reported that the main processing factor affecting the mechanism of fluorine release is the amount of water vapour in the kiln atmosphere, the greater the amount, the greater the amount of fluorine released. Control of the amount of water vapour in an open flame tunnel

kiln is virtually impossible and so to attempt this is not considered a viable option for limiting the amount of fluorine released. In fact work done in this project under task A has shown that as soon as there is any water vapour in the kiln atmosphere the release of fluorine increases dramatically from the release in a dry atmosphere. Laboratory experiments carried out by TNO on a clay indicated that the fluoride emission was 265mg kg^{-1} fired product but when the same clay was fired in a tunnel kiln the emission appeared to be only 26mg kg^{-1} fired product. This difference has subsequently been observed for other clay types. It can be partly explained by the thickness of the emitting samples, 27mm laboratory specimen 210mm bricks. This means that in practice the diffusion path for HF and H_2O is longer on the factory than in the laboratory and as a result the emission will be lower. However, the very large difference in HF emission indicates that this explanation alone is not sufficient and another phenomenon is taking place in a tunnel kiln, reabsorption of HF which is in fact a much more important process governing eventual kiln emissions.

This might involve the reaction between calcic minerals, usually calcite, and the hydrogen fluoride in the kiln atmosphere to form calcium fluoride. Since the amount of calcium carbonate in a raw material mixture can be controlled, this reabsorption process has been seen as a useful method of minimising the fluoride emissions. Therefore, a second part of the study of the mechanism of fluoride release has been to look at the stability of calcium fluoride in the processing of clay containing raw materials and to apply these findings to the operation of a continuous firing process.

Thermodynamic considerations have shown that chemical bonding of the fluorine in the form of calcium fluoride is a very stable one. It is thermally more stable than fluorine bonded into clay minerals at high temperatures. It has been shown in the laboratory that by increasing the concentration of HF in the kiln atmosphere, the absorption of this gas at low temperatures is increased. In an actual tunnel kiln the concentration of HF has been shown to vary along the length of the kiln, being high in the firing zone where the fluorine is being driven off the clay mineral and dissociation of calcium fluoride is taking place and low in the preheat zone where the fluoride is being absorbed due to reactions with the constituents of the unfired products.

It is below 700°C that this reabsorption takes place. It can take place in clays with low lime content as well as those with a high lime content. However, with low lime content clays the absorption is onto clay minerals and the bonding is weak and subsequently in the high temperature zones all the absorbed fluoride is re-emitted. In high lime clays the calcium fluoride formed is more stable and the re-emission of the fluoride is much less.

Much of the reaction is between the fluoride gases and the surfaces of the products in the preheat zone. If a body contains unreacted lime compounds in the firing zone, there is some reaction between fluorine released from the clay mineral and lime within the body. This fixes some of the fluorine before diffusion allows it to escape. This lack of diffusion due to density also will suppress the dissociation of fluorine released at higher temperatures leading to the fixation of that fluorine inside the product. Some of the fluorides formed on the surface by reabsorption will however dissociate at higher temperatures and this will increase the fluoride concentration in these zones. Increased concentration means increase partial pressure of HF which in turn means less dissociation of fluoride and so there is a balance achieved for a particular set of kiln conditions.

The study of the mechanisms of fluoride release have given rise to three courses of action for the lowering of emissions from tunnel kilns :-

- increase the contact between flue gases and heating products
- minimise gas flow through the emissions zone
- create stable chemical bonding of fluoride by using compounds which form fluorides with low partial pressures at high temperatures.

S4.5 Fluoride Abatement Additives

At the commencement of the project, it was agreed that any additives must not adversely affect the properties of the product such as compressive strength, water absorption, durability, soluble salts contents, liability to efflorescence, appearance (primarily colour) and etc. The use of additives should require only minimal modifications, if any, to the production process for potentially successful use. Finally the cost of purchasing the material, its preparation and making the addition should not add an unacceptable amount to the manufacturing costs. As a guide to this amount a typical cost of purchasing, maintaining and operating a scrubber can be £3-£4 sterling per thousand bricks. If the purchase of a scrubber can be avoided this money would be available to purchase and process the additive.

The survey of suitable additives revealed three groups :

- (i) Fluoride reactive compounds :- these react with the fluoride released by the clay mineral to form a more stable compound that can survive the high temperatures of the firing process.
- (ii) Fluxes :- these materials can lower the temperature at which vitrification commences and increase the rate of vitrification so reducing the residence time of the product above 900°C.
- (iii) Inert diluents :- additives that can be mixed with the clay which contain no fluoride compounds and hence effectively reduce the fluoride content of the mixture.

S4.5.1 Fluoride Reactive Compounds

These must have the capability to react with fluorine and the resulting compound must be stable at high temperatures in an atmosphere that contains water vapour. The best known one of these compounds is calcium carbonate, CaCO_3 . Below about 800°C the carbonate will react with hydrogen fluoride gas to give calcium fluoride, water and carbon dioxide. Above this temperature the calcium carbonate begins to dissociate to give lime and carbon dioxide but the hydrogen fluoride will still react with the lime producing calcium fluoride and water. The calcium fluoride is fairly stable at high temperatures and, as has already been described in the section of this report on the mechanism of fluoride release, it only needs a low partial pressure of hydrogen fluoride to prevent the dissociation of the calcium fluoride.

A search of the data on single fluoride compounds has been carried out and from a thermodynamic point of view there are only three stable fluoride compounds, the fluorides of calcium (CaF_2) strontium (SrF_2) and barium (BaF_2). Barium carbonate is already used as an additive in the industry for the prevention of soluble sulphate scum and it is interesting to note its capabilities regarding the reduction of fluoride emission. However, from a cost basis and

as will be seen from the quantities required the only viable additive for fluoride abatement is calcium carbonate.

S4.5.1.1 Laboratory testing of the fluoride reactive additive CaCO_3

Reference has already been made in the work reported under task A that intermittent kiln firing reveals only a minimal effect or no effect at all of calcium carbonate on fluoride emission. This is most probably caused by the fact that the firing process in these kilns constantly supplies fresh atmosphere and there is no build up of hydrogen fluoride concentration and hence no partial pressure due to this gas. Therefore at high temperatures any calcium fluoride formed does not have its decomposition suppressed. To counteract this effect experiments were undertaken firing test pieces in the TNO laboratory kiln in a hydrogen fluoride containing atmosphere. The test pieces produced were from Weald Clay and Keuper Marl both with and without a 1.8% by mass addition of calcium carbonate.

During these experiments the flue gas flow was only $1\ell \text{ min}^{-1}$ and this low flow resulted in the complete absorption of the hydrogen fluoride fed into the kiln by all the samples. However, the samples containing the calcium carbonate continue absorbing the hydrogen fluoride to a higher temperature than those without the addition and their emission rate is lower in the high temperature range. It can be deduced from these experiments that calcium carbonate is an effective additive for reducing fluoride emissions. It also emerged from these experiments that when the temperature dropped after the firing process all the samples started absorbing fluoride again.

S4.5.1.2 Pilot Scale Testing of Additives

Since preheat reabsorption of fluoride does not take place in a intermittent kiln, these trials were carried out to provide an indication of the product properties to be expected if limestone additions were to be made in a factory. The emission of fluoride effects were only indicative qualitatively and not at all reliable quantitatively. The Etruria Marl and Weald Clay were studied, the former had two 1% and 5% by mass of calcium carbonate added to it and the latter 0.5% and 2.5% by mass. Bricks from each mixture plus bricks from each clay alone were fired separately in the large laboratory intermittent kiln. The fired bricks produced were sampled and tested for water absorption, linear shrinkage, weight loss and compressive strength. A continuous record of fluoride emission was made and recorded in graphical form.

There was a marked increase in water absorption and decrease in strength with the Etruria Marl samples containing limestone. A 1% addition resulted in a 26% increase in water absorption and an 11% decrease in compressive strength. The 5% limestone addition resulted in a 52% increase in water absorption and a 28% decrease in compressive strength. There were decreases in linear shrinkage and increases in weight loss too.

Whilst the resulting physical properties were within the claimed specification for these bricks, the changes in property were considered to be of such magnitude that the long term durability of these products may be doubtful.

The property changes in the Weald Clay bricks with additions were much smaller and not definitely all in the same direction. The 0.5% limestone addition resulted in a 12% increase

in water absorption and a 2% decrease in compressive strength, this latter result being within the limits of experimental error. The 2.5% limestone addition again produced an increase in water absorption of 2.5% and surprisingly an increase in strength of the same amount, both of these changes being within the limits of experimental error. These results were considered to show little or no change in the properties of products from this clay with these limestone additions.

There was a reduction of about 9% by mass total fluoride emission if limestone was added to the Etruria Marl with a reduction of up to 20% in peak emission concentration at the 5% limestone addition level but it has to be remembered that no reabsorption has taken place.

There were reductions in fluoride emission of approximately 6% and 9% by mass respectively for the 0.5% and 2.5% limestone additions to the Weald Clay but only about a 7% reduction in peak emission concentration for both additions. This last value is within the limits of error of the measurement technique.

S4.5.1.3 Industrial Trials

These trials have been reported under the task A section of this report. Sufficient to say here that 0.5% addition to the Etruria Marl at UK2 factory produced only a marginal effect on the fluoride emission. A trial carried out at factory IRL3 had a much more marked effect. The limestone used was high purity, 98% CaCO₃, and very fine, less than 58µm. A 1.75% by mass addition of it to a mixture of 75% Carboniferous Shale and 25% asphalt sand reduced the concentration of hydrogen fluoride in kiln exhaust gases from 18 to 5 mgm⁻³ when firing under oxidising conditions and 20 to 3 mgm⁻³ when firing under reducing conditions, all concentration values quoted are corrected. The magnitude of these reductions, 72 and 86%, in fluoride concentrations are the largest observed in this project particularly for such a small addition of limestone.

S4.5.2 Fluxes

The work undertaken regarding fluxes has been a literature review using an international bibliographical database. Based upon the criteria agreed for the suitability of additives quoted in S4.5 above the following were identified as possible fluxes :-

- Carbonaceous Material
- Pulverised Fuel Ash (PFA)
- Ceramic Sludge
- Blast Furnace Slag
- Sewage Sludge and Sludge Ash
- Glass Cullet
- Auxiliary Fluxes

Carbonaceous materials act as fluxes by reducing iron compounds in the naturally occurring clays from ferric to ferrous state and it is the reduced iron compounds which will melt at lower temperatures. However, clays containing naturally occurring carbonaceous material would be unsuitable for using further additive of this type and even clays with nil or very low carbonaceous content may not be amenable to the use of this additive since the product colours

would almost certainly be changed. The currently marketable product would become unsaleable. Also often tunnel kilns built for carbonaceous material free clay firing are of insufficient length to accommodate the extra time that would be needed to oxidise the carbonaceous material during the firing in order to avoid bloating. The extra oxygen needed to oxidise the carbonaceous material would also mean increased secondary airflow through the kiln, a condition which could preclude an increase in the fluoride concentration in the firing zone, a feature that has been shown elsewhere in this report to suppress the evolution of fluorine from the clay.

A number of studies of the effectiveness of PFA additions as a flux have shown that it can be successfully used. This material is a completely non-plastic one and therefore some clays that are lacking in workability would not be capable of absorbing sufficient quantities of it. Work carried out by others has shown that in order to be used successfully a long term supply of fine consistent quality of PFA is required. It is an attractive additive from an environmental viewpoint, it is finding a use for small quantities of a potentially waste material.

Whilst ground blast furnace slag can act as a flux in a clay body it is probably its high CaO content that is of more value as an absorber of fluorine from the kiln atmosphere.

Probably the most promising flux for reducing fluoride emissions is coloured glass cullet. This is again a waste material whose use in heavy clay products would be an acceptable recycling route which would have the additional benefit of potentially reducing fluoride emissions from the firing of clay. Quantities of ground cullet added and the grinding of the cullet would be clay specific and being completely non-plastic its use in clays lacking workability could be limited. Much more work on a production scale than was possible in this project requires to be done to fully assess the effectiveness of this material on the reduction of fluoride emissions but the indications are promising.

S4.5.3 Inert Diluents

Whilst inert fluoride free diluents were initially considered as possible suitable additives early laboratory work undertaken as part of this project indicated that the fluorine content of the original raw materials had little effect on the fluoride emission. Therefore unless inert diluents are substituted in very large quantities their use will have little bearing on the emission from kilns. Process variables and the chemistry of fluoride containing compounds in the clay are far more important in this respect. It is now therefore obvious that there is no benefit in using inert fluoride free diluents simply because they are that alone. If they have another effective property such as a flux then their use should be considered.

This project has confirmed that the additive material with the greatest potential for reducing fluoride emissions is limestone. This is due to the ease and speed with which fluorine reacts with calcium carbonate and the greater thermal stability of the resulting calcium fluoride when compared with the fluorine bearing clay minerals. The firing of clay products in a continuous kiln presents an ideal opportunity both in temperature and time for the fluoride in the kiln atmosphere to react with the calcium carbonate in the body in the preheat zone of the kiln. Detailed examination of this reaction and the optimum conditions needed to bring it about are given in this report and factory trials have confirmed the theoretical conclusions and laboratory findings.

S4.6 Dry Limestone Exhaust Gas Scrubber Control System

The object of the task D of the project was to develop a control system for the operation of dry limestone cascade system exhaust gas scrubbers by utilizing the continuous fluoride analyser to monitor the emissions up the chimney stack.

S4.6.1 Control System Operation

A system has been developed using a Eurotherm EPC 900 controller with inputs from a thermocouple, monitoring the temperature of the exhaust gases, and the continuous fluoride analyser. Outputs from the controller go to the starters of the limestone discharge worm and peeler system on the scrubber and to a visual display.

The thermocouple monitors the temperature of the exhaust gas from the scrubber and the controller checks this against the acid dew point preset limit. Should the temperature drop below that limit there is danger of acid condensation in the scrubber or stack and damage could occur to both. This limiting temperature, if reached, sets off an alarm function so that action can be taken to increase the exhaust gas temperature.

The signals from the continuous fluoride analyser are passed through a filter in the controller to prevent it reacting to spikes in the individual readings, it only reacts to an average value. The controller also records the number of times that the discharge worm and the peeling drum operate and using a preset quantity limit of discharge from the peeling drum totalises the quantity of limestone used.

S4.6.2 Trial Results

During the monitoring period no correlation between the concentration of hydrogen fluoride before and after the scrubber was found. The concentration measured after was however constant in spite of a variable incoming concentration.

The system successfully controlled the scrubber discharge and peeling mechanisms responding to variations in fluoride emission. However, a precondition imposed by the manufacturers for the successful operation of these towers is that the worm discharge taking limestone out of it and the peeler operation should be at a minimum of 20% of the total time. This effectively kept the fluoride emission level at less than 6 mgm^{-3} . Therefore no need arose for the controller to change the frequency of discharge and peeler operation. It was necessary to set a much lower limit to check the working of the controller. This was successfully achieved and the whole system worked as planned. However, of necessity this controller operation of the scrubber discharge and peeling system was of limited duration.

Mass balance calculations suggest a build up of calcium fluoride in the tower but because of mechanical breakdowns associated with the scrubber and unrelated to the control system, it was not possible to study this problem in the depth required.

A simple pay-back analysis of the scrubber indicates that the cost of operating the control system is high and needs a considerable reduction to make it an attractive addition to the scrubber. The biggest saving would be the availability of a much lower cost continuous

fluoride analyser. Provided that the current limits on fluoride emission to atmosphere remain and these scrubbers continue to function with the efficiency measured here, there seems no justification for such a control system. However, there needs to be available more published information on the long term efficiency of this type of scrubber. If the efficiencies decline markedly or the fluoride emission limits are reduced to have such a controller could become an advantage.

S4.7 Safe Disposal of Waste from Dry Limestone Flue Gas Scrubbers

This investigation of scrubber waste disposal was included in the project in an endeavour to close the circle from an environmental stand point by not replacing a gaseous waste with a solid one. In addition if it was not possible to find a use for the waste it was decided to carry out some experiments to determine the hazardous or otherwise nature of it.

S4.7.1 Mineralogical and Chemical Analysis

Waste material from four sources, two in the UK and two in The Netherlands were collected for this part of the project. XRD analysis of the samples revealed that calcite was a major constituent in all of them and calcium fluoride was a major constituent in only one of them, it was a minor constituent in the other three samples. Calcium sulphate was a minor constituent in two of the samples. XRF chemical analysis showed the predominant metal to be calcium as expected and sulphur as the other important constituent although an order of magnitude lower in amount. All the losses on ignition were high due to carbon dioxide from the unreacted carbonate and the fluorine from any fluoride present. The most important metal after calcium was iron but an average this was only 1/350th of the amount of calcium determined. Separate fluorine analysis revealed contents ranging from 1154 mgkg⁻¹ to 3150 mgkg⁻¹.

S4.7.2 Leachate Testing

With the possibility that scrubber waste could be put into landfill sites it was decided to look at the leachability of the waste in alkaline neutral and acid conditions. The test method used was in accordance with the German standard DIN 38 414 part 4¹. In the alkaline range a solution with hydrogen ion concentration (pH) 10 was used. In the acid situation in order to maintain acidity for 24 hours a 10% solution of acid, pH 0.10, had to be used. This was due to the high calcium carbonate content of the wastes neutralizing weaker acid solutions well within the 24 hour period. Even with these acid solutions the pH value had changed from 0.1 to 6.3 to 6.4 with three of the wastes after 24 hours and the fourth one had its acidity reduced by a factor of 10 but nevertheless was still noticeably acid. It can be seen that there was difficulty in maintaining acidity. Even in alkaline solutions the alkalinity tended to increase slightly in the 24 hour period.

ICP analysis of the leachates from all environments were carried out but the results from a neutral environment only were assessed in compliance with the European Council Directive on the Landfill of Waste, COM (93) 275 final SYN 335. This Directive lists the maximum permitted levels for elements. If any levels are higher than these then the waste is considered hazardous for the purposes of landfill. All of the elements, 18 in total including the heavy metals, in these leachates were at lower levels than the maximum permitted and the wastes can

therefore be considered as non-hazardous and are suitable for disposal into a landfill licensed to accept domestic refuse.

The European Waste Catalogue contains a list of all possible types of waste. The relevant category is "Waste arising from the manufacture of ceramic goods" code 10 12 00, the relevant sub-category being 10 12 05 "sludges from gas treatment". This sub-category is not marked as hazardous waste and can therefore be regarded as non-hazardous. The chemical testing of the leachates from the dry limestone flue gas scrubbers undertaken in this project supports the European Waste Catalogue classification of this material as being non-hazardous.

S4.7.3 Dry Limestone Scrubber Waste Disposal by Recycling

With its large unreacted limestone content it was considered reasonable to survey all industries which use calcium carbonate as possible outlets for this waste. Most of those reviewed require limestone of high purity and/or very white in colour. These criteria rule out the use of scrubber waste as a substitute for calcium carbonate. There is a possibility that it could be used in glass, ceramics and metal industries but it is likely that their processes would cause the re-release of fluorine, so transferring a problem from one industry to another. The most likely areas of use would be as fillers in the construction and plastics/rubbers/adhesives industries and as a source of fluorspar. From a survey of these industries, it seems that filler applications most likely to accept scrubber waste are bituminous products such as roof shingles, roll felt and asphaltic coatings, plastics eg outer core cover of PVC sheathed cables and cheap rubber products such as car mats. However, the quantities available, small from any one source, and their dispersal could well make collection and delivery transport costs inimical to its use.

A desk top review of the possible use of the material as a possible source of fluorspar was undertaken. This has resulted in the conclusion that it is not feasible to recover fluorite from scrubber waste using the mineral processing techniques. Practical work and evaluation by fluorspar processors has found that the particle size of the fluorite is many orders of magnitude too small. Chemical recovery of the fluorite can produce high purity material but there are effluent disposal problems with the waste solutions and it is more economic to use purer mineral fluorspar as the base for producing high purity fluorite.

S4.7.4 Re-use in the Heavy Clay Industry

One of the disposal/recycling routes to emerge from the literature survey was the potential use of this material in the ceramic industry. A number of experiments have been carried out to investigate the possibility of incorporating the scrubber waste back into the heavy clay products.

A laboratory trial was carried out using Keuper Marl clay from UK3 factory. Small briquettes were produced from the clay alone, clay plus 1% scrubber waste, clay plus 0.2% ground scrubber waste and clay plus 1% ground scrubber waste and 0.5% anti scumming agent. All percentage additions were by mass and all the ground scrubber waste was less than 500 μ m (<500 μ m). These briquettes were dried in clean air and fired in a factory kiln.

Limeblowing was seen on those containing unground scrubber waste, scumming was evident on all samples containing 1% scrubber waste although on the samples containing anti

scumming agent it was nowhere near as pronounced as on the others. The samples containing the 0.2% ground scrubber waste showed a trace of scum around the edges but generally their colour was as bright as those made with clay alone.

This experiment has highlighted two problems with the incorporation of scrubber waste into the products. Firstly the need to ensure that the waste is finely ground to avoid limeblowing and secondly the possibility of scumming of the product. This latter possibility will vary according to the sulphate content of the waste and the processing conditions used in the manufacture of the product.

A small trial was carried out at UK4 factory by making a 0.1% addition by mass of ground scrubber waste to the clay. The quantity of scrubber waste was the addition necessary to dispose of all of it produced at this factory. The bricks to which it was added fired to a cream colour which effectively made the assessment of scumming impossible but there was no detrimental effect on the physical properties of the bricks containing the addition when compared with those without it. The duration of the run was too short to assess the affect on fluoride emissions.

A theoretical exercise based upon the use of scrubber waste in a Dutch factory which adds limestone to the clay mix shows that, using their waste disposal costs, a saving of more than 50% can be achieved annually if one sums the fresh limestone costs and the waste disposal costs when there is no waste addition and when waste is added. This exercise concluded too that only some 0.11% addition by mass of scrubber waste needs to be added to the clay to dispose of all that produced and that this small quantity should not affect the colour of red bricks.

A scrubber waste addition trial was carried out at NL6 factory. Here 25% of the 7.7% limestone addition was replaced by scrubber waste the amount necessary to dispose of the waste if added on a regular basis. This level of addition also makes allowance for the calculated extra fluoride emission generated if continuous waste additions were being carried out. Two important indicators came from this trial. It takes a long time for equilibrium fluoride emissions to be established once the addition has been commenced, weeks rather than days. If scrubber waste is to be disposed of in this way about 50% of the additional fluoride added to the clay is retained in the product, due to the greater thermal stability of the calcium fluoride.

Therefore it seems that the continuous inclusion of scrubber waste in the product, even allowing for the cost of grinding it, is a cost saving way of disposing of it on a routine basis.

Reference:

1. DIN 38 414 Part 4. Sludge and Sediments (Group S) Determination of Leachability by Water (S4).

CHAPTER S5

CONCLUSIONS

S5.1 The aims of the project have been achieved. They were to develop a better understanding of the fluoride release mechanism occurring in the manufacture of heavy clay products and to investigate through laboratory, pilot and full scale production trials a series of low cost process modifications which will achieve a reduction in the amount of fluoride pollution into the atmosphere from continuous kilns firing such products. In addition the aims included the seeking of information to show how hazardous was the solid waste produced from dry limestone flue gas scrubbers, its best disposal option and the feasibility of automatic control of such scrubbers.

S5.2 The prior development of the continuous fluoride analyser proved to be the essential pre-requisite for the success of this project. Without it, it would have been impossible to monitor the effects on fluoride emissions of process modifications. The output from the equipment gave continuous realtime results as the experiments progressed. The accuracy and operational reliability has been proven.

S5.3 The theory of the mechanism of fluoride release has been clarified and validated by laboratory experiments and industrial trials. This has led to a fuller understanding of the mechanisms involved in fluoride abatement by process modification.

S5.4 All process modifications tested have been relevant, simple, practical and low cost and capable of being applied to existing kilns. The data and information obtained in this project can also be applied in the design, construction and operation of new kilns used by the industry.

S5.5 Effective abatement techniques have been shown to be :-

- use of fluoride reactive additive (eg. CaCO_3)
- increase reabsorption of fluoride in the preheat zone of the kiln by lengthening that zone or increasing turbulence and hence contact between gases and unfired product in that zone.
- utilise exhaust gases in pre-heaters.
- minimise gas flow through the firing zone.
- increase production.

S5.6 Calcium carbonate is the best most economical fluoride reactive additive to incorporate in a clay body to minimise fluoride emission. It will react with fluoride released within the clay body and with that in the kiln atmosphere in the kiln preheat zone - reabsorption, and the resulting calcium fluoride has good thermal stability so being difficult to breakdown in the firing zone.

S5.7 The emission of fluoride from a continuous kiln exhaust is the difference between the amount released from the clay in the firing zone and the amount reabsorbed in the preheat zone.

S5.8 Fluoride emissions from intermittent kiln firings in mass terms are always much higher than from continuous kilns when both are firing to a common schedule. This is due to there being no reabsorption process taking place in an intermittent kiln. The result of this fact can cause small scale laboratory firings in intermittent kilns to give unreliable quantitative results on the effect of fluoride emission abatement techniques.

S5.9 In production situations it is unlikely that any one abatement technique will suffice to bring about a significant lasting lowering of fluoride pollution from a kiln. A combination of techniques will almost certainly have to be applied. That combination will be kiln specific and very probably product variety specific.

S5.10 The reliance on concentration of fluoride per unit volume as a measure of pollution often masks true pollution level changes. Mass values either in terms of mass per unit time or unit material processed are the only true measure of the effect of changes in pollution levels. Some of the abatement techniques tried have shown little or no reduction in fluoride concentration in the exhaust gases but in reality there have been considerable reductions in terms of mass emitted. Table S5.1 gives abatement techniques monitored on industrial kilns during this project together with the magnitude of the change in mass of fluoride emission found. By noting the magnitude of the changes and their consistency one can obtain an indication of the more effective process changes found.

S5.11 Since all the abatement techniques are process related their applicability can be translated to some other sectors of the ceramic industry.

S5.12 By experimentation it has been shown that dry limestone flue gas scrubber waste is non-hazardous verifying its European Waste Catalogue classification. This means that it could be disposed of to landfill sites licenced for the disposal of domestic refuse.

S5.13 It has also been shown that a satisfactory disposal route for dry limestone flue gas scrubber waste is to grind it to a fine powder and incorporate this into the clay being used to make the products. The grinding is necessary to prevent the development of "lime-blowing" a defect in products caused by expansive particles of lime causing chips to appear. This disposal route can be easily achieved since the mass of waste produced is small compared with the mass of raw material being processed and so its effect on all aspects of product quality are insignificant.

S5.14 On line automatic control of the operation of dry limestone flue gas scrubbers has been shown to be possible by using the continuous fluoride monitor. However, the high cost of the monitor makes the payback period based upon reduced limestone use very long.

Table S5.1 The Effect of Process Modification on HF Emission Criteria

Action	Emission Criteria	Situation Before	Change / %
Push Rate Case 1 - 28.6% Increase	Concentration (mg m ⁻³)	103	+ 6
	Mass Flow (kg h ⁻¹)	2.63	+ 14
	Specific Emission (mg kg ⁻¹)	402	- 19
Push Rate Case 2 - 20.0% Increase	Concentration (mg m ⁻³)	38	+ 3
	Mass Flow (kg h ⁻¹)	0.73	+ 2
	Specific Emission (mg kg ⁻¹)	153	- 19
Time at Peak Temperature Decreased	Concentration (mg m ⁻³)	39	- 10
	Mass Flow (kg h ⁻¹)	0.74	- 10
	Specific Emission (mg kg ⁻¹)	124	- 10
Air Flow Reduce Fan Speed by 12.2%	Concentration (mg m ⁻³)	71	- 4
	Mass Flow (kg h ⁻¹)	2.35	- 16
	Specific Emission (mg kg ⁻¹)	310	- 16
Use of 55% Flue Gas in Preheater	Concentration (mg m ⁻³)	63	- 52
	Mass Flow (kg h ⁻¹)	0.83	- 52
	Specific Emission (mg kg ⁻¹)	254	- 52
Use of 100% Flue Gas in Preheater	Concentration (mg m ⁻³)	93	- 94
	Mass Flow (kg h ⁻¹)	1.07	- 94
	Specific Emission (mg kg ⁻¹)	273	- 93
Setting Pattern Change	Concentration (mg m ⁻³)	45	- 53
	Mass Flow (kg h ⁻¹)	0.17	- 47
	Specific Emission (mg kg ⁻¹)	48	- 42
Reduction Firing 8 Minutes During Last Stage of Push Period	Concentration (mg m ⁻³)	15	0
	Mass Flow (kg h ⁻¹)	0.43	- 5
	Specific Emission (mg kg ⁻¹)	46	- 7

Table S5.1 Continued

Action	Emission Criteria	Situation Before	Change / %
Additional Burner(s) in Preheat Case 1	Concentration (mg m ⁻³)	23	- 65
	Mass Flow (kg h ⁻¹)	0.25	- 52
	Specific Emission (mg kg ⁻¹)	73	- 56
Additional Burner(s) in Preheat Case 2	Concentration (mg m ⁻³)	97	- 53
	Mass Flow (kg h ⁻¹)	0.42	- 43
	Specific Emission (mg kg ⁻¹)	233	- 43
Additional Burner(s) in Preheat Case 3	Concentration (mg m ⁻³)	12	- 25
	Mass Flow (kg h ⁻¹)	0.14	+ 14
	Specific Emission (mg kg ⁻¹)	48	+ 7
Additional Burner(s) in Preheat Case 4	Concentration (mg m ⁻³)	122	- 86
	Mass Flow (kg h ⁻¹)	1.51	- 83
	Specific Emission (mg kg ⁻¹)	642	- 83
Addition of Limestone (Calcium Carbonate) Case 1 - +0.5%	Concentration (mg m ⁻³)	35	- 3
	Mass Flow (kg h ⁻¹)	0.70	- 4
	Specific Emission (mg kg ⁻¹)	142	- 4
Addition of Limestone (Calcium Carbonate) Case 2 - +1.75%	Concentration (mg m ⁻³)	17	- 71
	Mass Flow (kg h ⁻¹)	0.96	- 71
	Specific Emission (mg kg ⁻¹)	171	- 71
Addition of Limestone (Calcium Carbonate) Case 3 - +10%	Concentration (mg m ⁻³)	15	- 75
	Mass Flow (kg h ⁻¹)	0.43	- 67
	Specific Emission (mg kg ⁻¹)	46	- 67
Addition of Limestone (Calcium Carbonate) Case 4 - +15%	Concentration (mg m ⁻³)	7.6	- 62
	Mass Flow (kg h ⁻¹)	0.21	- 62
	Specific Emission (mg kg ⁻¹)	26	- 62

Acknowledgements

The three partners, CERAM Research, TNO, Forbairt, who undertook this project would like to thank the Directorate General XII Science Research and Development of the European Commission for the fifty per cent funding of it. Without this generosity the project could not have been undertaken. Coupled to this thanks we would like to add the name of Dr. J. Büsing, the project officer from the Directorate.

The partners would also like to thank the following who between them as industrial sponsors provided most of the remainder of the funding, the Brick Development Association in the UK, NOVEM (Netherlands Organisation for Energy and Environment), EuroCeramic BV and Desimpel Europe in the Netherlands and, Forbairt and Laggan Holdings Limited in Ireland. The following companies supported the project in kind by allowing the industrial trials to be undertaken on their factories, Ibstock Building Products Limited, Hanson Brick Limited, Marshall Clay Products Limited, Desimpel Europe, NBM Amstelland, Kingscourt Bricks Limited, Flemings Fireclays Limited, Redland Tile & Brick Ltd and these contributions were essential to the successful completion of this project.

Finally, but by no means least, the partners would like to thank all the staff of their respective organisations who contributed in any way to the successful operation and administration of the project. In particular we should just like to mention A. Lowe and M. J. Burton of CERAM Research, J. de Jong and Mrs. M. van den Acker of TNO and J. Murphy of Forbairt.