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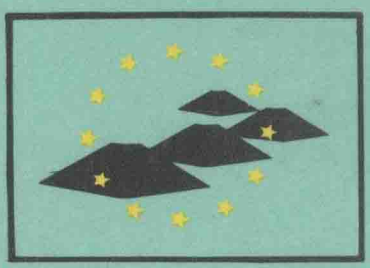

COAL - WATER MIXTURES

Edited by
P.F. SENS and J.K. WILKINSON

ELSEVIER APPLIED SCIENCE

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Commission of the European Communities, Brussels, Belgium

ELSEVIER APPLIED SCIENCE
LONDON and NEW YORK

ELSEVIER SCIENCE PUBLISHERS LTD
Crown House, Linton Road, Barking, Essex IG11 8JU, England

Sole Distributor in the USA and Canada
ELSEVIER SCIENCE PUBLISHING CO., INC.
655 Avenue of the Americas, New York, NY 10010, USA

WITH 20 TABLES AND 35 ILLUSTRATIONS

British Library Cataloguing in Publication Data

Coal–water mixtures.
1. Fuels. Fluidised combustion
I. Sens, P. F. II. Wilkinson, J. K. (James Keith), *1933–*
III. Commission of the European Communities, *Directorate-General for Science, Research and Development.*
621.402′3

ISBN 1-85166-323-1

Library of Congress CIP data applied for

Publication arrangements by Commission of the European Communities, Directorate-General Telecommunications, Information Industries and Innovation, Scientific and Technical Communications Service, Luxembourg

EUR 11846

Printed in Great Britain by Galliard (Printers) Ltd, Great Yarmouth

COAL–WATER MIXTURES

Proceedings of a contractors' meeting organized by the Commission of the European Communities, Directorate-General for Science, Research and Development, held in Brussels, Belgium, 26 May 1988.

PREFACE

The present volume represents the second publication from the energy R&D programme "Utilization of Solid Fuels", performed under the supervision of Directorate-General XII for Science, Research and Development of the Commission of the European Communities. This programme started with a call for proposals for R&D projects in March 1985 and, at present, 66 projects are in progress. Some of them are now approaching termination, others will continue into 1989 and even 1990, although 1988 is formally the last year of the current energy R&D programme.

The "Utilization of Solid Fuels" programme addresses the following issues :

- fluidized bed combustion
- coal/water mixtures
- burner development
- solid fuels in integrated cycles
- environmental aspects
- transportation and handling
- basic studies of solid fuel combustion and properties.

On May 26, 1988, a contractors meeting on the subject of coal/water mixtures took place in Brussels, where progress in this area was reported from nine projects. The reports prepared for this meeting are compiled in this book.

The meeting provided a forum for interesting discussions and exchange of views and experience.
At the end of the book, some conclusions are given as well as some directions for future work.
This is of special interest now because of discussions, taking place at this moment, concerning the contents of the next energy R&D programme, to start in January 1989.

P.F. SENS

C O N T E N T S

Generic Studies

Ultrasonics spectroscopy of CWM fuels

ULTRASONICS SPECTROSCOPY OF CWM FUELS

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Contract number : EN3F-0017-UK

Duration : 27 months
1 April 1986 - 30 June 1988

Total budget : ECU 133262 CEC contribution: ECU 133262

Head of project : Mr G.J.L. GRIFFIN

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Summary

We report on work carried out on applications of ultrasonic techniques to CWM fuels. A theoretical basis for the use of ultrasonic techniques in the measurement of such parameters as flow velocity, solids content, and average particle size was proposed by Davis (1) in 1978; however our experience has indicated that the operation of these techniques in real systems offers problems not all of which are apparent from the theory. We have set up apparatus for making pulse velocity and attenuation measurements over a range of frequencies with the option for making broad-band measurements followed by computer spectral analysis of the output. At low frequencies (circa 200Hz) we have studied the proPerties of shear waves in CWM and in this paper we present these results with a qualitative explanation of the development of elastic rigidity in the slurry. We have dealt with the known sensitivity of the acoustic properties of materials to temperature changes by very precise temperature control and measurement, but our system would be amenable to adaptation to simultaneous temperature and acoustic measurement with real-time computer correction of the data. Such a system, could form the basis of a non-invasive pipeline device for the continuous observation of CWM properties provided that enough data is collected on the variations in the acoustic properties of coal itself.

1.Objectives.

The basic physics of concentrated suspensions is not well developed and, consequently, there is a weak theoretical base for the development of measurement technologies and the formulation of mixtures with defined properties. Ultrasonic spectroscopy provides a method for the study of the microscopic physical properties of these systems when

used in conjunction with other physical techniques.
The principal objective of this project was to develop apparatus capable of making spectroscopic measurements on suspensions in general, and CWM in particular, over the frequency range 1-100 MHz. In parallel with this, developments of the theory of sound propagation in such systems have been made to permit interpretation of the data and render the results of practical analytical value. It was also hoped that the results would help in the development of practical plant instrumentation suitable for monitoring the operations of coal milling, CWM compounding, and CWM storage.

2. Introduction

This paper reports work carried out to investigate the microstructure and dynamics of coal-in-water suspensions as part of a programme of studies on the physical properties of concentrated suspensions. A common characteristic of such materials is their opacity, which makes the use of optical probes, e.g. dynamic light scattering , difficult or impossible. We originally conceived the idea of using ultrasonics as a means to probe the local particle density so as to study the complex process of sedimentation in concentrated suspensions. It appeared that such techniques would also be useful, possibly as an in-line probe, in investigation of the microscopic properties of CWMs, materials which were interesting technologically and of considerable potential economically.
Nuclear or soft X-ray gauges might be used provided that sufficient contrast between the continuous phase and the suspended coal particles could be obtained, but this could be difficult through the walls of a tank. On-line density measurement (by vibrating U-tube) might be useful but only gives one parameter. This leads to the conclusion that ultrasonic measurements could be the most versatile, probing simultaneously, the density, elasticity, viscosity and other characteristics derivable from the acoustic propagation constants of the medium.

A practical CWM can be made to contain 70 percent coal, one percent of stabilising additives and the remainder water. The mixture then comprises a weak gel capable of supporting the smaller particles indefinitely and slowing down the rate of sedimentation of the larger particles under gravity to give stability for a few days at least. When the mixture is sheared it exhibits non-Newtonian behaviour: the viscosity varies with the rate of shear. Such a CWM will have lower viscosity at higher shear rates, making it easy to pump and the mechanism of this phenomenon lies in modification of the gel structure. In flow this structure is subject to two competing processes of formation and shear induced dissolution so that while a high shear rate reduces the viscosity, the process is reversible and the gel structure recovers when the shear rate is reduced. This type of behaviour is classified as pseudoplasticity.

If the coal loading is too high, particle contacts begin to occur and it is possible for the structure to lock up, at least locally. The mechanism of deformation requires the dilation of locked regions to get things moving and the behaviour is therefore known as dilatancy. A practical CWM has excess water to prevent dilatancy and the delicate balance in the formulation between high coal content, stability and fluidity clearly requires careful control. Even a given mixture may change with time due to changes in the coal surface properties, particle attrition or temperature change. A system of on-line insrumentation and control to maintain the slurry in its optimum state might therefore be an ultimate objective.
The description so far has assumed that the structural changes take place instantaneously. This is not the case and the time dependent or relaxation processes comprise the fundamental microscopic mechanisms from which the macroscopic rheology derives. When the time scale for the microstructural relaxation process is sufficiently long (greater than 1 millisecond, say) this will be apparent in the viscosity at a given shear rate being a function of time. The classical way to demonstrate this is by running an experiment first with increasing shear rate and then decreasing. Time dependency will be exhibited as a hysteresis loop in a plot of viscosity vs. shear rate. If the loop is generated in a clockwise sense, as would be typical for CWM, the material is described as thixotropic. (The case of an anticlockwise loop is called rheopexy). Fast relaxations are not revealed in such experiments and it is in this area where ultrasonic spectroscopy becomes a valuable tool.

The present report is divided into four sections, Materials and Methods, where a brief account of the handling and preparation techniques adopted in our laboratories is given, Ultrasonic Measurement Techniques where the development of hardware for measuring ultrasonic propagation parameters in concentrated colloids is described, and Shearometric Measurements, where experiments on the elastic properties of CWM are reported and an interesting anomaly in the temperature dependence of the shear modulus is discussed. A brief discussion of our ultrasonic measurements with reference to Davis's theory (1978) is given in conclusion.

3. Materials and Methods.

Materials were supplied to us either as filter cake, that is to say a solid product with low water content coming from a wet milling and froth flotation plant, or as ready prepared CWM samples. Most of the successful commercial fuel trials have been made with coals that suit the CWM process, rather than with difficult soft porous coals and the samples provided for our work have come into the former category. Much of what is reported here was

derived from work with WK (Widow Kennedy) coal filter-cake or CWM supplied by Carbogel AB. These samples were studied by light microscopy and some typical photomicrographs are appended. Attempts to demonstrate simple particle shape similarities in these coal particles by using image analysis to obtain L:D ratios, and form factors were, inconclusive the fracture shapes probably being fractal in nature.

In the case of the filter cake materials it was necessary to disperse them in de-ionised water with the addition of dispersing and suspending additives which were supplied to us as coded samples. This operation was carried out originally using a laboratory stirrer but the operation was very time consuming and, with larger quantities, we used a Transfermix single-zone screw mixing machine as designed by Frenkel. This machine features a patented screw geometry which combines controlled high shear combined with excellent transfer mixing. It proved very effective for dispersing CWM although originally designed for use in the dispersion of textured paint formulations.

The CWM samples, having been wet processed by the suppliers, already contained proprietary stabilisers and no attempt was made by us to modify this component of the CWM Only the water content was adjusted by drying out or addition of de-ionised water with appropriate stirring. Evaporation is a significant problem, where storage quantities of 1kg and sample quantities as small as 1gm are used, simply due to the large surface area to volume ratio. Consequently it was found necessary, for each experiment, to carry out a moisture determination by drying small samples to constant weight in a vacuum oven. The difficulty in controlling the moisture content during measurements was an obstacle to making series of measurements on a consistent and well-characterised material. A specialised case where this restriction may be overcome is referred to below. The effects of moisture variation were most marked at the highest solids loading and therefore in the materials with the greatest practical potential. In order to maintain slurries in a suspended condition over a period of days or weeks, containers were stored horizontally on a set of slowly rotating rubber rollers. This resulted in some heterogeneity, with mobile slurry in the bulk, but a static film adhering to the container walls. This, again, is a problem associated with handling small quantities of material and is a potential source of variability in the material.

The special case of highly consistent samples was a research tool, having no obvious practical applications. It involved replacing the aqueous continous phase with a polymerisable gel to immobilise the coal particles. The resulting sample was a stable two phase solid having consistent properties over time and allowing reproducible measurements to be made. The propagation of elastic waves

through a viscoelastic matrix containing suspended coal particles could be studied with this system and is relevant to CWM in which the gel strength is not exceeded. The Stokes´ viscous resistance is absent (at least for the larger particles) and this allows hypotheses about the effects of scattering alone on the acoustic attenuation to be tested. The samples do not flow on an experimental timescale.

The gel formulation which was adopted for this application was acrylamide-methylene bis-acrylamide copolymer in aqueous solution, polymerised using a mixture of TEMED (NNN´N´ tetramethylethylene diamine) and ammonium persulphate.

4.Ultrasonic measurement techniques.

4.1 Prototype single transducer rig.

This apparatus was based on the design of Bradfield (2) in which a single transducer acts as transmitter and receiver. Standard PZT immersion probes set the dimensions of the seating for the probe and we found that the polished cylindrical housings of these probes were sufficiently accurately dimensioned for them to be retained in a simple bored hole through a brass disc at one end of which an O-ring was fixed in a groove by a compression ring. The epoxy resin coated face of the probe formed the bottom of the experimental cell so that the adjustment mechanism for the reflector face could be conveniently situated with the micrometer unit above the reflector rod. The sample cell was set upon the base and comprised a length of cast acrylic tube which was seated on a shoulder machined on the periphery of the brass disc holding the transducer. A little RTV silicone sealant made a reliable joint at this part of the assembly, although when working with CWM a light smear of silicone grease was found to be perfectly adequate.

The reflector plate was the lapped and polished end of a 12mm diameter stainless steel rod whose upper end was held in a simple split collet which was pulled upwards against the tip of the adjustment micrometer by means of a single compression spring. This arrangement made possible a smooth vertical adjustment of the reflector without backlash, although its length did permit a small degree of lateral wobble which could be seen to disturb the signal amplitude by a few dB. This rig , in conjunction with a standard commercial pulser-receiver (an Ultrasonoscope Mk.10) enabled us to perform basic experiments and generate data and experience of great value in designing and setting up the high frequency rig and the ultrasonic tank. The simplicity of the equipment meant that measurements could be carried out quickly and, therefore, no attempt was made to control the temperature of the apparatus apart from keeping it in a draught free environment and storing the materials and apparatus together for some time before

a measurement session in order to allow equilibration to room temperature.

4.2 Short path, high frequency rig.

Working with frequencies in the 1 to 50 mHz range means that the rigidity of the main framework of the apparatus must limit movements to less than the acoustic wavelength of the pulses in water at those frequencies and, therefore, a massive cast iron plate was adopted as the base and reference plane for the apparatus. Because the sample cell contains liquid and is most conveniently operated with a single liquid seal it follows that the base plate must be arranged with its reference plane parallel to the vertical axis of the sample cell which is also the axis of the acoustic pulse transmission system.

It was decided at an early stage that the most manageable scheme for introducing the pulses into the liquid samples and then accepting them for transmission to the detecting transducer was to use very precisely manufactured fused silica cylinders with plane ends finished to optical standards. With these rods 15mm in diameter and, typically, 100 mm long, a solution had to be found to the problem of holding the rods accurately coaxial without damaging or introducing stresses into the silica. Furthermore at least one rod had to be capable of precise and reproducible translation along the signal transmission axis in order to vary the pulse path length in the experimental liquid. The linear motion was arranged to operate on the upper rod. Because it could not be assumed that the acoustic and mechanical axes of the rod system would coincide it was thought prudent to allow for a degree of fine angular adjustment of the lower, fixed, rod and this was done by inserting a circular, kinematic tilting table between the lower cylinder clamp and the supporting framework. The tilting table was designed especially for this apparatus as no standard type could be found. It depended for its action on three adjusting jack screws of very fine pitch (80 t.p.i.) situated around the periphery of a circular table and bearing upwards against a second similar table supporting the silica cylinder clamp and drawn to the lower table by appropriate springs.

In order to ensure that the cylinders and their clamps could be demounted and reassembled without disturbing the alignment of the apparatus both the upper and lower assemblies were retained in standard engineering tapers (number 3 Morse) which had been precision ground into the upper and lower support structures respectively.

The problem of providing a precise linear motion for the upper silica rod assembly was solved by adopting a standard commercial linear ball bush device mounted in a "pillow block" of the kind normally used for supporting machine shafts. These recirculating ball bushes were available in a form in which the shell , and also the support block, were both cut along one radius in such a manner that screw adjustment across the narrow cut allowed

for the diameter of the shell to be minutely adjusted. It was thus possible to produce a linear motion system of extremely low friction (the manufacturer's claim a friction coefficient of 0.004 or better) with almost zero lateral slack. Chrome steel precision hollow shafting was available for these standard ball bushes and was used to make the main upper and lower structures with the lower shaft being clamped in a simple split static clamping block having the same centre height as the active bearing bush of the upper unit. The upper shaft was also clamped to an external frame carrying the return springs which overcame the weight of the upper system and kept it gently pressed against a standard screw micrometer mounted above the apparatus. The exact position of the upper silica rod was monitored by an optical linear displacement transducer made by the Heidenhain Company and capable of showing the position of the upper rod to within one micron on a remote digital display. This combination of screw micrometer, linear ball bearing, return springs, and linear displacement transducer worked extremely well in practice and no mechanical disturbance due to its functioning could be detected in the signal detection circuitry.

The problem of clamping the silica rods was solved by adopting the standard engineering practice of using collets, which are very precise in their clamping action, and do not generate local pressures on the silica cylinders. It was found possible to purchase collets and matching collet adapters for mating with the number three Morse tapers that had been ground in the main hollow support shafts and simple threaded brass draw-tubes were made for pulling the collets into position.

4.3 Ultrasonic tank rig.

The short path rig described in 4.2 above worked very well but it was not suitable for working at lower frequencies (less than 5 MHz) because of problems with diffraction. We also wished to work with transducers made using PVDF (poly(vinylidene difluoride)), piezo-electric films and these could not easily be accommodated in the usual transducer mounts. It was decided, therefore, to design and construct a water tank system with the operating axis horizontal and the transducers submerged. This meant that a reasonable degree of temperature control could be achieved by treating the tank (a Perspex box about 700mm long and of 210 mm square end aspect) as a thermostat bath using a standard laboratory temperature control unit and stirrer. The problem of submerging a liquid sample in such a bath was solved by building a series of Perspex cylindrical cells about 70mm diameter and of various lengths, with their ends sealed by a taut PVDF film. This (commercially available) material is extremely thin and has an acoustic impedance close to that of water; in control experiments with the cell containing water it was not possible to detect the presence of the