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A REVIEW OF THE APPLICATIONS OF RECENT DEVELOPMENTS OF NMR IN MATERIALS SCIENCE

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NMR spectroscopy has developed dramatically in the last decade or so and has expanded into two new areas which have very exciting potential to materials science. These new areas are the high-resolution NMR of solids and NMR spin imaging. Examples are given where both these techniques have been harnessed to provide information hitherto difficult or impossible to obtain for such materials as coal, cements, minerals, catalysts and polymers.

1. Introduction

Nuclear magnetic resonance spectroscopy is a branch of science which continues to expand in terms of its applicability and it provides us with information that is often unique in wide-ranging areas such as geology, chemistry, physics, fuel technology, lubrication and materials. This paper contains two main themes: solid-state NMR, and NMR spin imaging; their enormous scope for application in solids and materials science will be reviewed.

High-resolution solid-state NMR, the first theme, is a fairly recent development, only really coming to commercial fruition in the 1980's, thanks to a combination of technological developments. Once one can produce routine high-resolution spectra of solids, a whole vista of applications opens up, possibly wider in scope than for liquids, and examples will be given of the unique contribution to be made in areas such as polymers, coal, minerals, glasses, catalysts and cements.

NMR spin imaging, the second theme, is a still more recent development of NMR, and the fact that images of fluids in solids can be routinely

produced has already had a momentous impact in the field of medicine. The scope for non-medical applications is also of considerable interest and potential, and examples will be given of the use of spin imaging to study fluid flow or ingress of liquids into solid materials such as plastics, cements, sand and rocks.

2. Solid-state NMR

There are three main reasons why the production of high-resolution spectra from solids is technically difficult: the sensitivity of many important nuclei is poor; the NMR signals are inherently broader; and relaxation times can be long, leading to unacceptably long spectrum-accumulation periods. The details of these experimental difficulties and how they are solved are covered in detail in references 1, 2 and 3.

In short, the problems are solved using a combination of techniques. The sensitivity is improved by using higher-field superconducting magnets and, when one is studying isotopically dilute nuclei such as ^{13}C and ^{29}Si, isotope enrichment. The lines are narrowed by "magic-angle spinning" (MAS) and heteronuclear dipolar decoupling [2,3] (for dilute spins) or homonuclear decoupling [3] (for abundant spins). Relaxation times are shortened by cross-polarization techniques [4] or by the deliberate introduction of paramagnetic species into the sample [5].

2.1 Applications of solid-state NMR

By suitable choice of experimental conditions it is feasible to use solid-state NMR to study both surface and bulk phenomena of solids.

2.1.1 Surface studies In the case of Si NMR, the application of cross-polarization effectively filters out silicon species that are not within a few bond distances of ^{1}H species. In other words, Si NMR with cross-polarization is a means to study surface phenomena provided that hydrogen-bearing species, such as OH groups or organic species, are present.

The properties of silica gels are strongly dependent on the number of hydroxyl species at the surface and the silicon chemical shift of surface species of silica has proved to be a useful quantity to determine the number of OH groups attached to these surface species [6,7]. In addition, the cross-polarization times for $(SiO)_4Si$, $(SiO)_3SiOH$ and $(SiO)_2Si(OH)_2$ have been

reported [6] and it was clearly demonstrated that proximity of ^{29}Si nuclei to ^{1}H nuclei (in the hydroxyl groups) substantially shortens the cross-polarization time. Subsequent work on the reactivity of silica gels to hexamethyldisilazane [8] has resulted in a methodology to relate structure and reactivity, and Si NMR can be used to provide details of hydroxyl surface populations as a function of temperature [9]. Temperatures in excess of $1000^{o}C$, for example, are necessary to remove completely surface OH groups from silica gel. When such stringent dehydration steps have been taken, the rehydration process becomes less efficient compared to the case where lower temperature ($<500^{o}C$) dehydration has been performed. Si NMR has provided evidence [10] for the mechanism of the hydration process in terms of singly and doubly hydroxylated silicons at the surface.

One of the important and valuable aspects of cross-polarization is that it allows one to study surfaces almost exclusively and to monitor chemical and structural changes accordingly. The presence of surface silanol groups has been detected [11-13] for various zeolites and their role in ring closure together with the beneficial effect of NH_4^+ counter ions has been reported [11].

^{13}C NMR too is a powerful means to study surfaces. An example which demonstrates this is shown in Figure 1, in the form of a high-resolution cross-polarization MAS spectrum of a chemically bound surface species, in which all the six different carbon types in the species are clearly resolved. The relevance of such studies in catalysis is enormous [1].

2.1.2 Bulk solids studies Figure 2 gives an indication of chemical shifts and line widths of silicon spectra of some common silicious materials. Use can be made of the chemical shift range and the fairly narrow line of quartz to characterize silicon-containing minerals, as demonstrated by the aluminosilicates, which encompass a wide range of minerals, clays and both natural and synthetic zeolites. Figure 3 shows the basic structure and chemical shifts of aluminosilicates, the significance being the presence of Al atoms in the second coordination sphere. This is demonstrated in Figure 4, which shows the difference in the spectrum brought about by a simple difference in the Si/Al ratio. These spectra indicate what an excellent tool NMR spectroscopy is for examining the structure of minerals, both natural and synthetic, in a non-

destructive manner. A recent article gives an example of the combined use of Si and Al NMR to clays and provides further references [14].

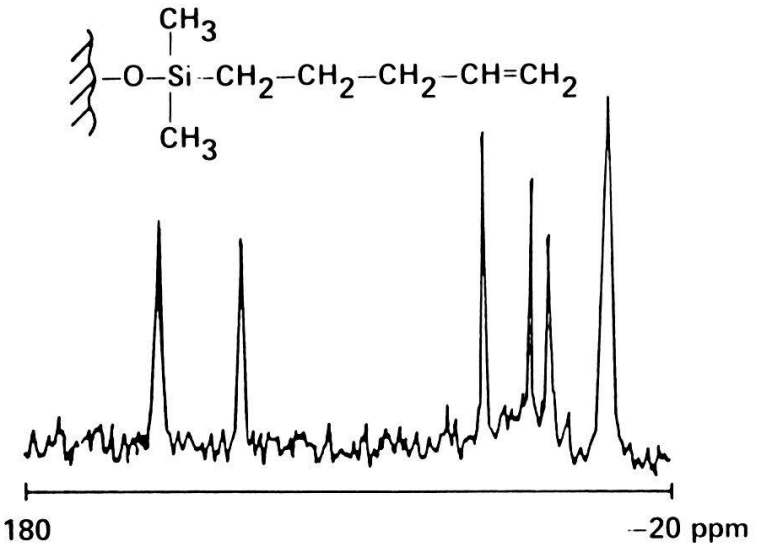


Fig. 1. ^{13}C NMR spectrum of chemically bound organic species on silica gel.

Another area where solid-state NMR promises to have an impact is in cements and concretes. Although these materials have been used for construction purposes for centuries, new applications are still being developed, and it remains desirable to have a better understanding of the hydration, setting and degradation processes. Interest has grown recently in the application of Si and Al NMR techniques to help us understand these processes [15-17]. Basically, it is possible using Si NMR to make assignments of the silicate species present and to observe the gradual appearance of oligomeric species as a function of time during the setting process. Table 1 gives chemical shifts of the different silicate oligomers. Using Al NMR the transition of tetrahedrally coordinated aluminium in anhydrous monocalcium aluminate to the octahedral form in the hydrated species can be followed [17].

Coal and coal ashes are complex materials. One important characteristic of coal - the aromatic carbon content - was almost impossible to measure

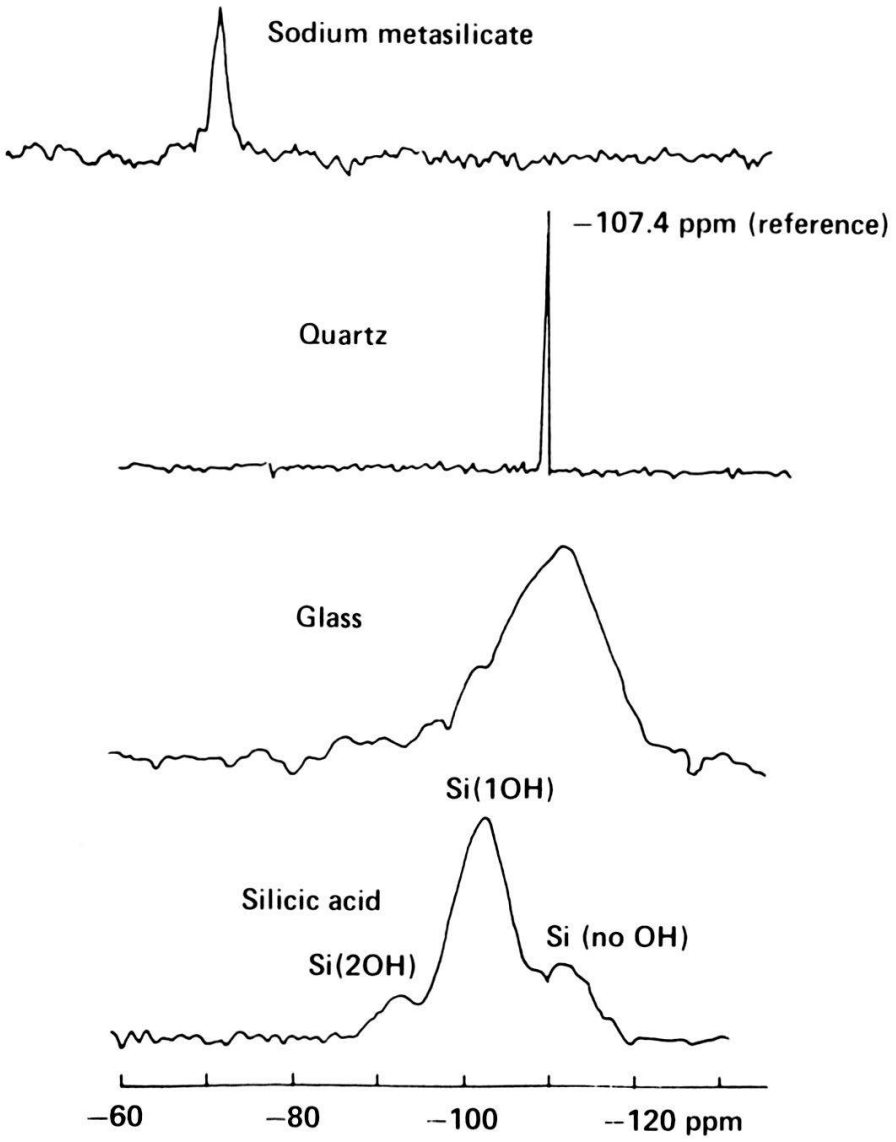


Fig. 2. Typical ^{29}Si NMR spectra of some common silicious materials

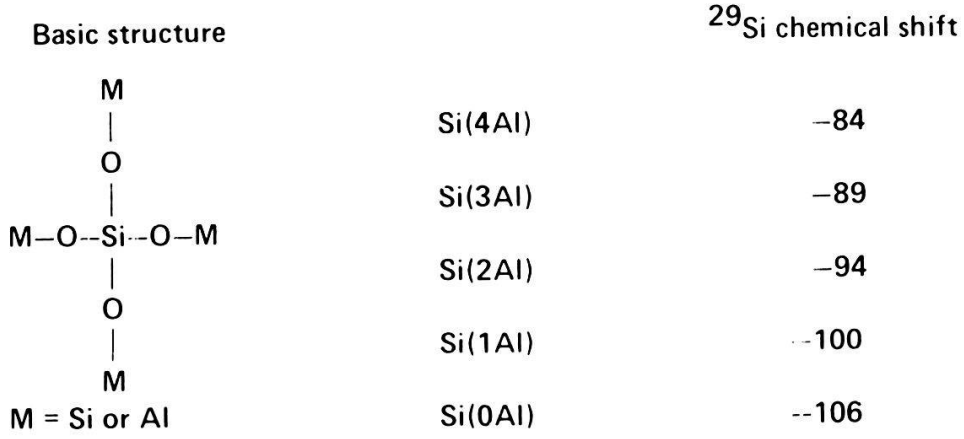


Fig. 3. Basic structure and ^{29}Si chemical shifts of the five possible structural units in aluminosilicates.

until magic-angle spinning techniques became available. It is now routine to obtain these aromaticities, as shown in Figure 5 for a representative selection of coals [18]. A further use of ^{13}C NMR is to follow chemical changes occurring in coal, as for example during oxidation when modified spectra will be produced corresponding to the formation of oxidized species.

Coal is sufficiently complicated that it even has an inorganic chemistry of its own. There is frequently 10% or more of ash in coal and this can have very important consequences in the ultimate use of coal. The ash content contributes especially to the coal's slag-forming characteristics and the abrasivity of the fly ash produced in large combustors. Any technique, therefore, which will provide information on the mineral composition of coal prior to burning will be potentially valuable. High-resolution NMR falls into this category, and this is illustrated in Figure 6, which shows two common minerals present in coal. Note how important it is to have a long pulse delay, necessitated by the very long silicon relaxation times in quartz.

The foregoing applications apply largely to inorganic materials, but a vast area of study of solid-state NMR is in organic materials, with special relevance to polymers. Some reference to this has been made by van der Klink in this journal [19] on the use of relaxation times to monitor molecular

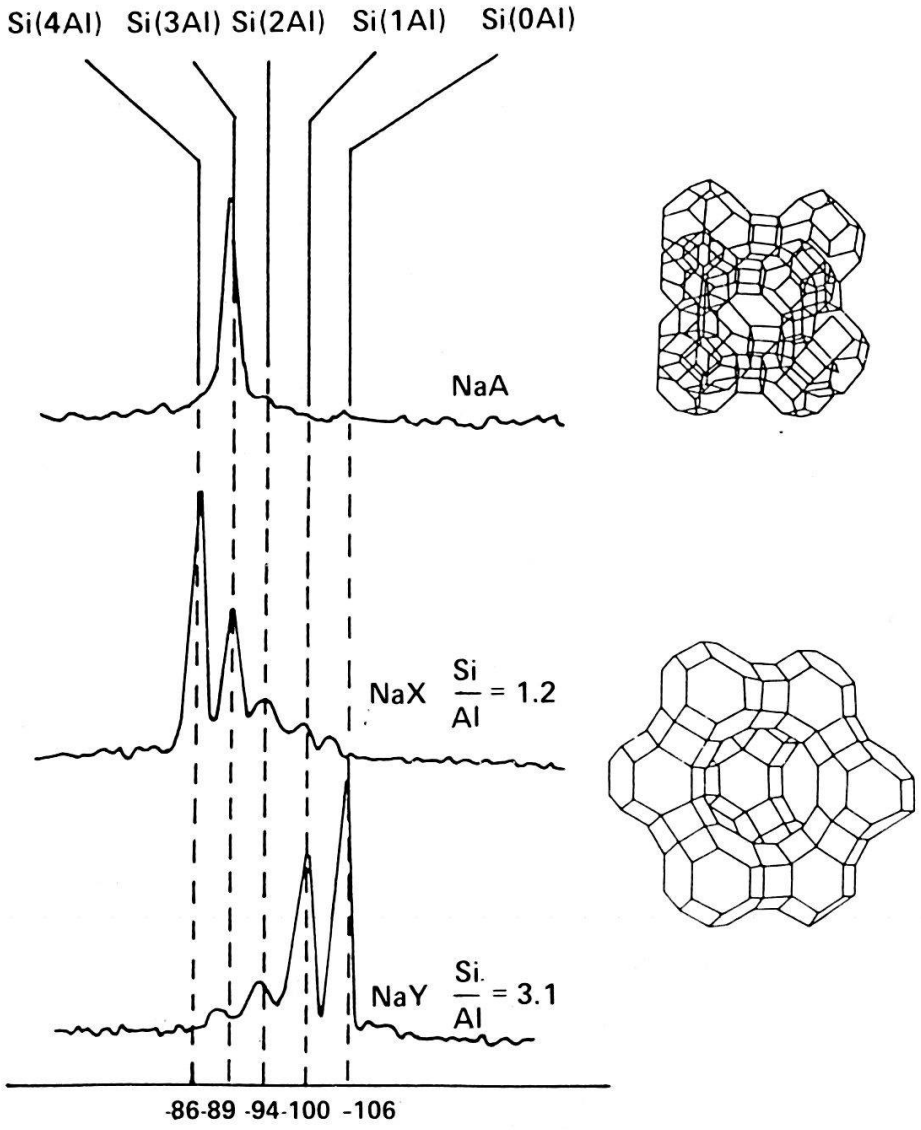


Fig. 4. Effect of Si/Al ratio on the ^{29}Si spectra of synthetic zeolites.

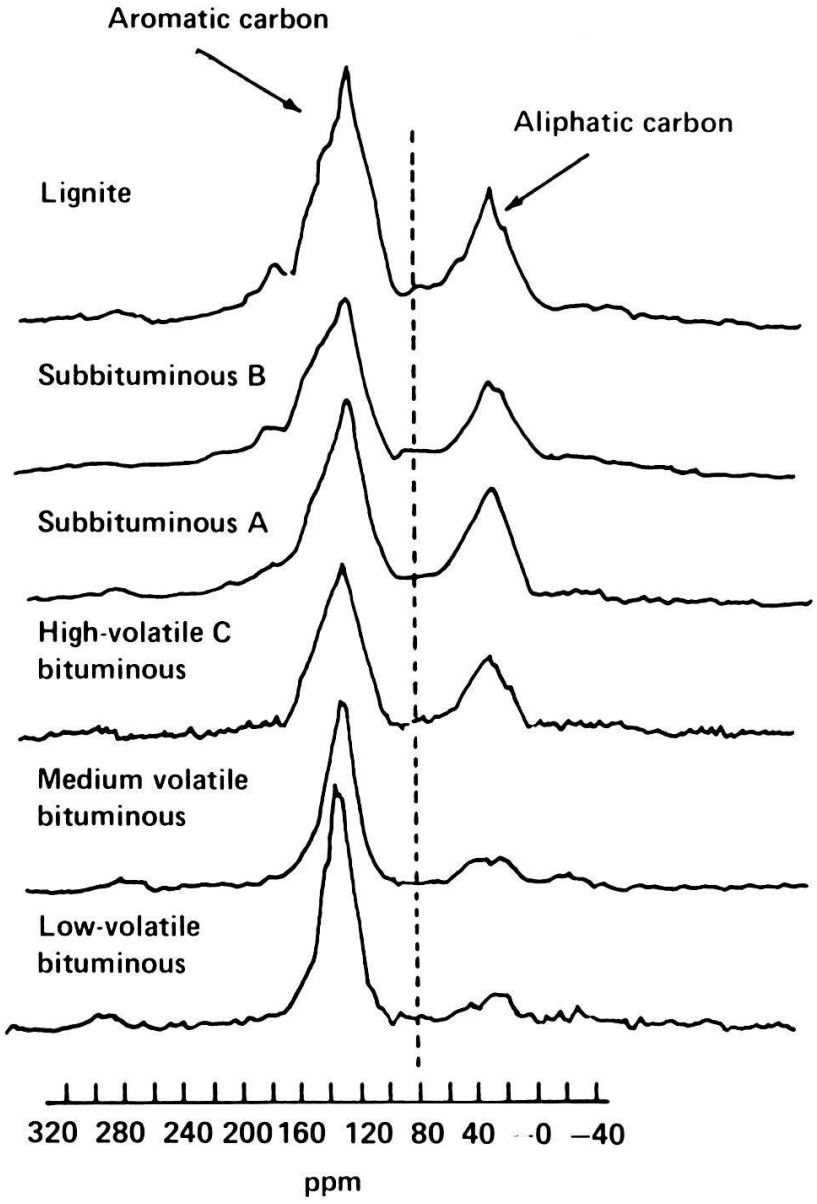


Fig. 5. ^{13}C MAS NMR spectra of coals of different rank.

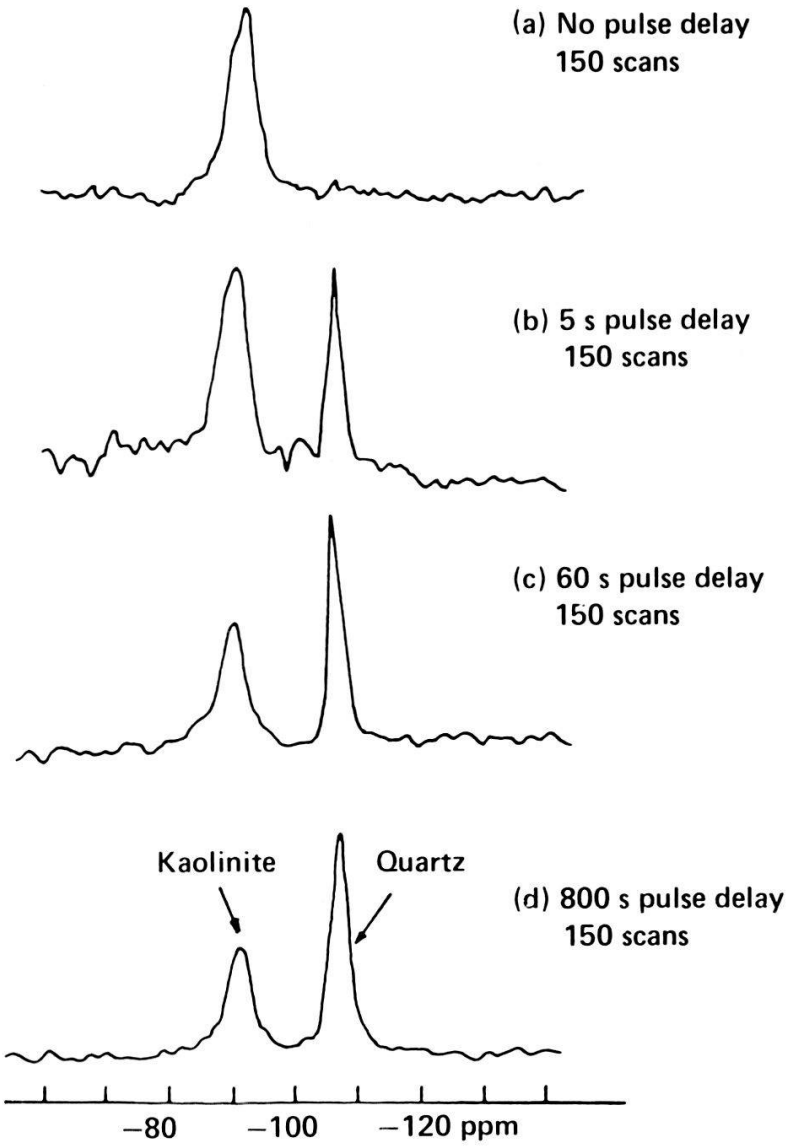
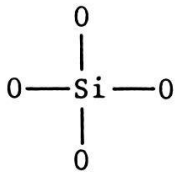
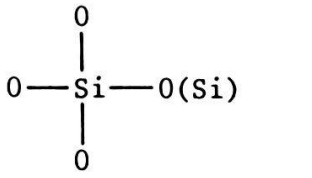
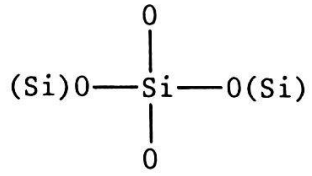
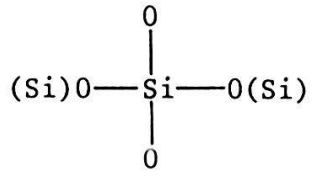
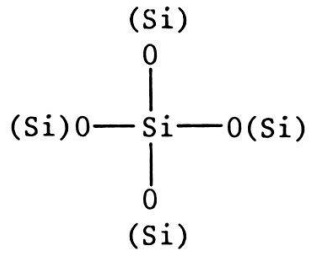


Fig. 6. Silicon NMR of coal minerals.

Table I

^{29}Si chemical shifts for different types of silicates*

Structure	Designation	Chemical shift range (ppm from Me_4Si reference)
 single tetrahedron	Q^0	-66 to -74
 end unit	Q^1	-77 to -83
 chain unit	Q^2	-86 to -88
 branching unit	Q^3	-90 to -100
 cross-linking unit	Q^4	-107 to -110

* Data and nomenclature from JACS, 1980, 102, 4889

motion in polymers and to help us understand their physical properties. Another aspect of NMR that illustrates the versatility and power of the technique to provide unique information on structures and composition is the chemical shift. Figure 7 shows that resolutions can be achieved using solid-state techniques that are equivalent to those obtained in solution for a vulcanized polyisoprene rubber, thereby providing a method for the identification and characterization of otherwise insoluble and intractable materials. A word of warning is appropriate here. If one wishes to extract quantitative information from spectra, it is essential to carry out relaxation-time studies, since these values can vary widely in cross-linked materials and lead one to make incorrect conclusions.

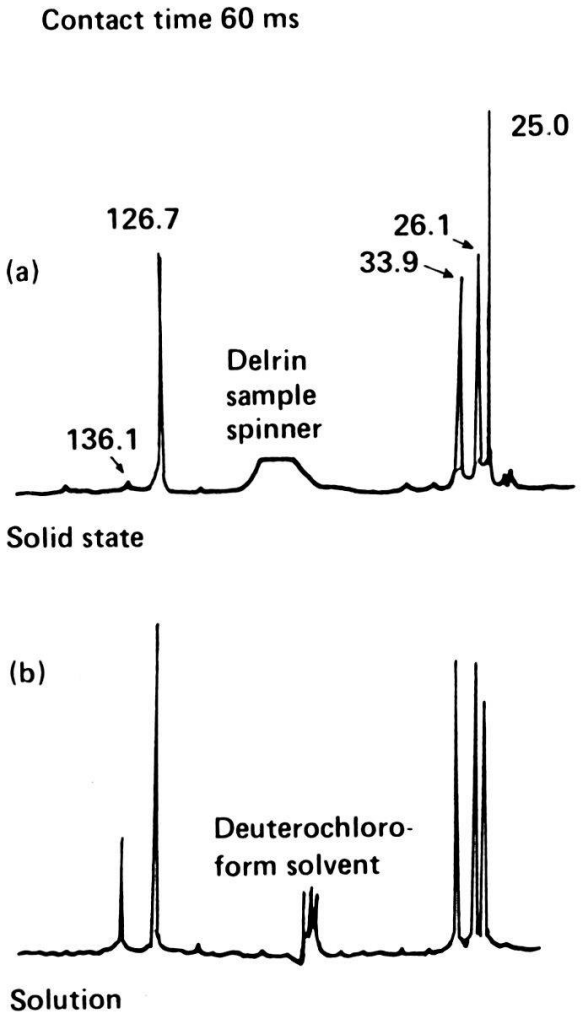


Fig. 7. (a) ^{13}C NMR spectrum of solid vulcanized polyisoprene (b) ^{13}C NMR spectrum of unvulcanized polyisoprene in deuterochloroform solution.

3. NMR Imaging

NMR imaging in materials is essentially a new development, in which a good deal of cross-fertilization will be required between the fields of materials science and NMR spectroscopy. Concerning the principles of imaging, one of the simplest methods is to build up a picture in a point-by-point way, just like a television image. In order to do this, a field gradient is applied across the sample so that different parts of the cross-section are brought into resonance successively, and for each picture element (pixel) the signal is stored. The signal is proportional to the density of the nuclei of choice (usually protons) in each pixel. The final image is then produced by presenting all the pixels simultaneously on a screen. A description of the various improved techniques for the production of NMR images and the underlying theory is given by Mansfield and Morris [20].

The application of opposing field gradients along the magnetic field allows one to produce images of thin slices of a sample. Spatial information can thus be derived from the slice of interest. The position of the slice along the sample can then be changed at will, allowing three-dimensional information to be derived from the sample.

3.1 Information from images

As was the case with solid-state NMR, one can make use of all the NMR parameters - intensity, relaxation times and chemical shifts - to provide information on the sample under study.

3.1.1 Spin density maps A spin density map is simply a picture built up from the number of spins - usually, but not necessarily, protons - and it will be one of the most useful means for enabling us to look at concentrations and distributions of fluids in solids, for example, moisture in cements, concretes, plastics, insulators, etc.

3.1.2 Relaxation time discrimination There are two relaxation times currently relevant to imaging: the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2. Very briefly, T_1 is a time constant for the process whereby excited nuclei release their energy to the surroundings (the lattice) as a result of interactions with local oscillating magnetic fields. T_2 is a time constant for the de-phasing of magnetization as nuclei exchange their energy with other spin systems, but without loss of energy. Measurement

of relaxation times is useful owing to the fact that their values are determined by the rate of molecular motion in a fluid. For example, we can use T_1 and T_2 values to distinguish between proton (or water) molecules with differing mobilities and much use has already been made of this in the medical field to study differences between cancerous and non-cancerous tissue.

3.1.3 Chemical shifts The chemical shift of a nucleus, in particular hydrogen and carbon, has been, and continues to be, one of the most useful and powerful observables in the field of analysis of molecular structure. As yet, the study of chemical shifts in NMR imaging is still in its infancy, in that there are technical difficulties that need to be overcome. It holds, however, great promise for the future.

3.2 Applications of NMR imaging

The object of this section is to give an impression of the potential of NMR imaging in the non-medical field.

3.2.1 Petrophysics One of the growth areas in the oil industry that will become extremely important in the twenty-first century is that of enhanced oil recovery, i.e. the technology of removing residual oil from porous rock. NMR imaging provides us with a non-invasive technique to look into the flow and diffusion behaviour of different fluids in rocks and sands, which, in turn, will provide guidance for finding the best method for removing this residual oil. A model system was built [21] containing tightly packed sand made up of bands containing crude oil alone and various oil-and-water mixtures. NMR images of 2-mm thick "slices" along the length of the tube were then measured. The objective here is to see (a) whether we can distinguish between the two different fluids, oil and water; and (b) how much of each is present. A simple spin density map of fluid concentration alone would obviously be insufficient in this case. The particular crude oil used in this experiment is more viscous than water, and thus has a shorter T_1 and T_2. Use was made of this difference to discriminate between the oil and the water. This is shown in Figure 8. The spatial resolution achievable is demonstrated by the image of a globule of oil buried in the moist sand, in section E of this sample and reproduced in figure 9.

3.2.2 Materials Two potentially important areas of application of NMR imaging in materials science are the study of the rate and degree of

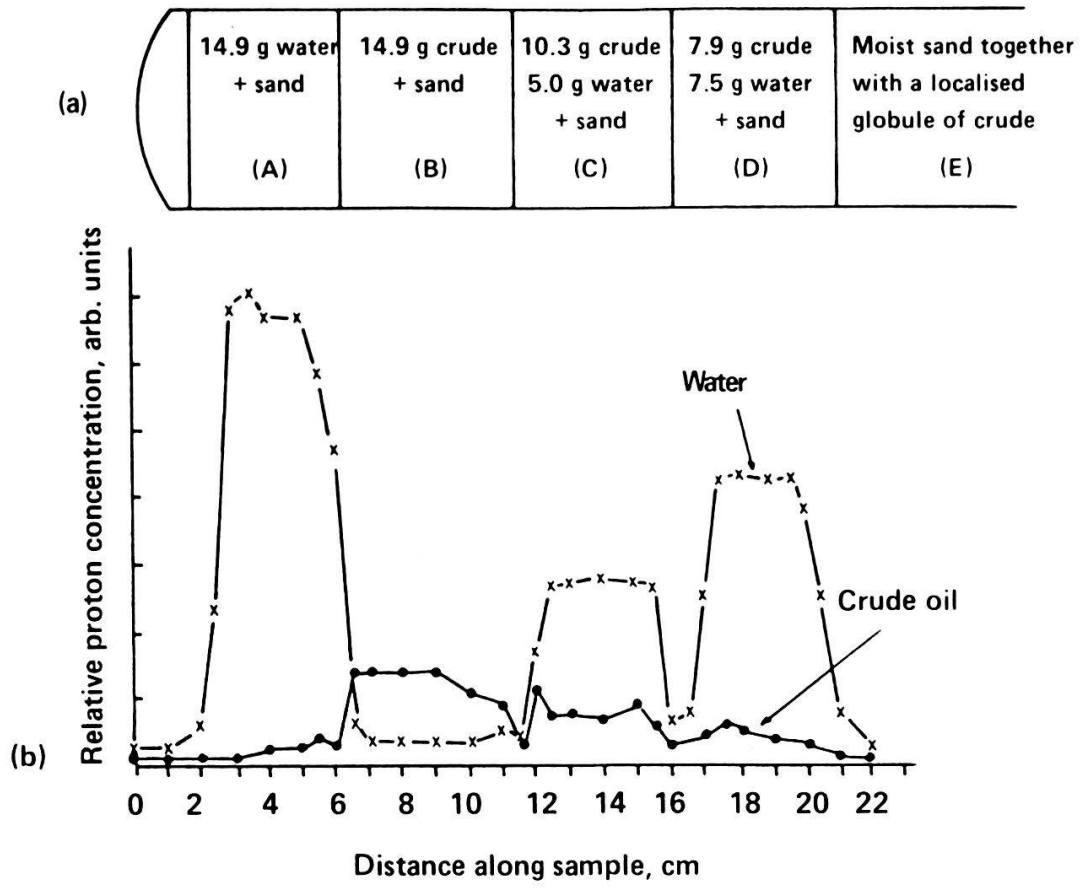


Fig. 8. Composition (a) and measured proton concentrations (b) of crude oil and water in a simulated core sample.

ingress of fluids into solids and the measurement of rubbery or mobile phases in solid matrices.

For many of the day-to-day uses of materials such as polymers the ingress of fluid is highly undesirable. It can lead to deformation and chemica deterioration of the material with consequent loss of mechanical strength and resistance. The non-destructive nature of NMR imaging will be of immense value in the investigation of fluids/solid systems. Nylon, for example, is frequently used as a sealing material in valves and joints, where it comes into contact with a variety of fluids. Any uptake of these fluids can be detrimental to the sealing properties of the nylon. Experiments performed by Mansfield [22] have shown that a nylon surface that has been exposed to hot

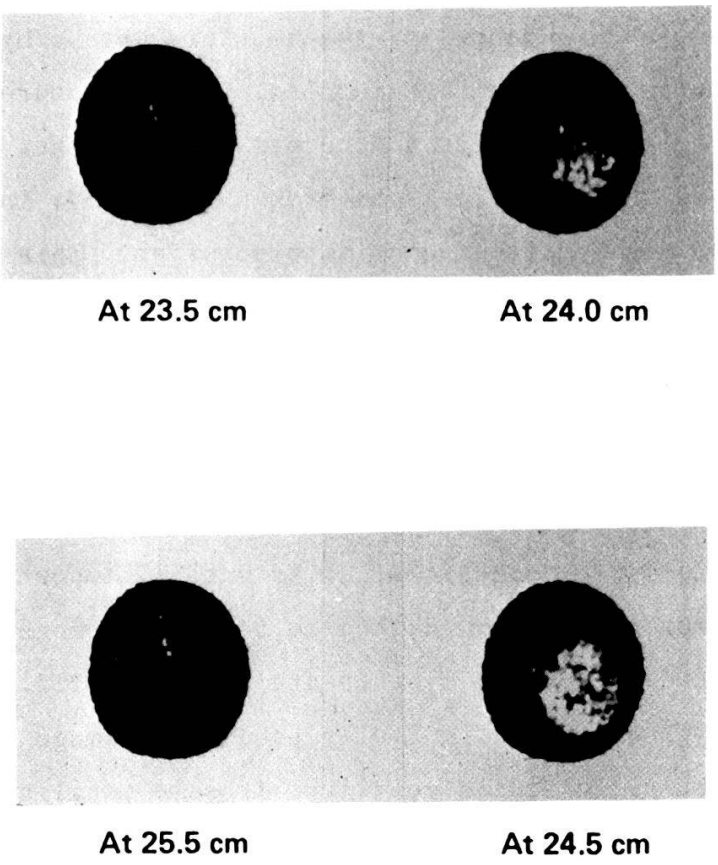


Fig. 9. Proton density maps along section (E) of the simulated core sample. The darker shade corresponds to water, the lighter to crude oil.

water for a period of several days takes up a substantial amount of water. NMR imaging provides an accurate profile of the degree of ingress of the moisture and the diffusion coefficient of water into nylon can be calculated. Thus, quantitative rather than qualitative (or merely visual) information can be derived.

Similar experiments have been performed in order to study the ingress of fluid into various polymeric materials, such as epoxy resins and polyurethane foams. In the case of epoxy resins, unlike nylon, there was no smooth profile of decreasing water content as one progressed along the cross-section of the sample towards the centre. Instead, pockets of moisture could be de-

tected along the cross-section, [23,24] indicative of the presence of micro cracks. This represents a promising new method for the detection of such faults in the material.

Ingress studies are by no means limited to organic polymers. For example, images have been produced of the moisture uptake by concrete [23,25]. Here, it is of interest to note that ingress of the moisture occurred preferentially into the original skin of a concrete block, rather than into a surface freshly exposed when the block was broken open [25]. In other words, a fresh surface is not as hygroscopic as an old surface. This represents an area worthy of further study in the search for the causes of degradation of cementitious materials in hostile or aggressive environments.

3.2.3 Molecular mobility discrimination Nowadays, we are moving more and more towards the use of polymers or composites to replace metals which for weight or cost reasons are less desirable. As new materials are tested, and this applies especially to composites, it is vitally important to know whether the material is homogeneously mixed, and to test for homogeneity without destroying the material. Composite systems are totally solid: there is no fluid present and NMR imaging does not normally produce an image for solids unless there is some degree of molecular mobility. If some mobility can be introduced, by raising the temperature for example, then an image may be produced of the mobile components in composite materials and then the questions of homogeneity and the migration of components can be studied. Preliminary but highly encouraging data have been produced for a sandwich made up of layers of rigid polymer and elastomeric polymer [23], the latter having sufficient molecular mobility to produce an image when heated to a temperature above its glass transition temperature but below its melting point.

4. Conclusion

Dramatic developments are now taking place in two areas of NMR: solid state and NMR imaging. Both have extremely exciting and promising consequences in the study of solids and materials sciences. In solid-state NMR we have a new tool to enable us to identify the chemical structures in solids, such as glasses, minerals, polymers, cements, catalysts, and to follow chemical changes in such materials in a non-invasive way. With NMR imaging we

have at our disposal a means to look inside materials, again non-destructively, and to look at the motional behaviour of fluids therein, their chemical composition, and even the amount of different fluids.

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