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ELECTROMAGNETIC RESONANCE BOREHOLE ASSAY LOGGING

Prepared for

UNITED STATES DEPARTMENT OF THE INTERIOR
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by

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TELEDYNE GEOTECH

FINAL REPORT

on

Contract No. JO265024

STUDY CONTRACT FOR THE IDENTIFICATION OF TECHNOLOGIES TO SUPPORT THE APPLICATION OF ELECTROMAGNETIC RESONANCE TECHNIQUES IN BOREHOLE LOGGING.

January, 1978

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16. ABSTRACT

This was a study to identify and evaluate known technologies employing electromagnetic resonance phenomena in solid minerals for their identification and assaying, particularly assay logging of exploratory boreholes. A comprehensive literature search and study revealed some little known NMR (nuclear magnetic resonance) techniques developed by Professor G. J. Béné's group at the University of Geneva, Switzerland. These are suitable for use in weak, inhomogeneous magnetic fields. Laboratory NMR tests of numerous U.S. ore minerals showed good identifying signals from phosphates, fluorspar, bauxite, oil shale, and spodumene (lithium) ores, but not from the copper, lead, antimony or manganese ores tested. Use of EPR "signatures" for such ores is suggested. A conceptual design for an NMR assay logging system is proposed.

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FOREWORD

This report was prepared by Teledyne Geotech, Garland, Texas under USBM Contract Number J0255024. The contract was initiated under the Advancing Mining Technology (Metal and Nonmetal) Research Program. It was administered under the technical direction of DMRC, with Mr. George Schneider acting as the Technical Project Officer. Mr. R. J. Simonich was the Contract Administrator for the Bureau of Mines.

This report is a summary of the work recently completed as part of this contract during the period June 25, 1976 to December 28, 1977. This report was submitted by the authors on January 6, 1978.

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1. INTRODUCTION AND SUMMARY

1.1 PURPOSE

This report describes an exploratory research program to "identify and evaluate the feasibility" of appropriate borehole logging techniques to assay (identify and measure) crystalline minerals by electromagnetic resonance (EMR). The EMR phenomena under consideration have included nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR)--also called electron spin resonance (ESR), and minor types such as nuclear quadrupole resonance (NQR) and ferromagnetic resonance (FMR). All these effects have been discovered, and the body of science based on them has been developed, since about 1947. Readers of this report are expected to have some initial familiarity with NMR and EPR.*

Specific objectives of the program outlined by the Bureau of Mines included the investigation of two major questions previously encountered** in applying EMR methods to borehole logging:

(1) How can a high-strength, highly uniform, magnetic aligning field be applied to the rock surrounding a borehole?

(2) How can the observation of the weak, broad-line EMR spectra from solids be improved?

An even more fundamental question which we felt should be addressed was:

(3) What are the "indicator" substances in natural ores that will produce distinctive, diagnostic EMR effects (that is, strong identifying spectra)? (Most substances heretofore used in EMR research are high-purity synthetics.)

All three questions have been investigated and tentative answers found. Full experimental evaluation of proposed techniques has not been possible under this program.

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*There are several good introductory textbooks on these subjects, for example, "Nuclear Magnetic Resonance" by E. R. Andrew, Cambridge Univ. Press, 1969.

**These questions were brought up in a previous ARPA/Bu Mines research program to investigate the feasibility of borehole NQR logging to measure rock stress in situ (Teledyne Geotech Report TDY-20TR73-7, 1973).

1.2 RESULTS OF THE RESEARCH

The organization of this report is shown in the table of contents. The details of the study are given in subsequent sections 2 through 5; many readers will not be interested in such details. Hence, the findings of the program are briefly summarized in the following listing.

(1) Direct assaying by NMR has been shown feasible for the following important American industrial minerals:

(a) The phosphorus content of all important U. S. phosphate rocks.

(b) The fluorine content of Nevada fluorspar ore.

(c) The lithium content of North Carolina spodumene ore.

(d) The aluminum content of Arkansas bauxite ore.

(e) The recoverable oil from Colorado oil shale.

(2) Many other industrial minerals which do not give an identifying NMR effect from valuable elements should have a distinctive EPR "fingerprint" which may be useful for assaying. Two such minerals have been shown to give this indirect effect:

(a) A Utah galena/sphalerite (sulfide) ore.

(b) A Utah zinc/lead/silver/molybdenum (oxide) ore.

(3) Magnetic field strengths of a few hundred to a few thousand gauss can be produced within the rock around a borehole out to distances of the order of a few borehole diameters, either by massive permanent magnets, or by powered coils with or without cores. The latter can produce time-modulated fields, but require substantial power and cooling accessories. Superconducting magnets can produce only steady fields, stronger than those of permanent magnets, but at much higher cost.

(4) Magnetic fields uniform to within a few percent can be achieved over a sample volume comparable to that of the adjacent borehole by means of transverse loop or magnet arrays. This degree of uniformity may be sufficient for the spectra of solids, for which line widths may be several percent of the resonance frequency or field.

(5) Swiss scientists at the University of Geneva, under the leadership of Prof. George J. Béné, have invented several techniques for NMR in weak, non-uniform magnetic fields which appear to be ideally suited to the logging application. All involve a secondary magnetic field which is periodically reversed to cause re-assembly of the precessing group of nuclei, so that a series of pulse-echoes is produced. These techniques have not yet been applied to solids, but have been used for samples outside of the test coils. One related technique is disclosed in a 1962 Chevron patent.

(6) The broad resonances from solids can be sharpened and increased in size by forcibly driving the nuclei near resonance with strong ac fields (at least several gauss). A multiple-pulse program is generally used and may improve the spectral resolution by factors up to 1000. Several oil-industry companies have patented proton-logging techniques employing driven resonance. A second method of line-narrowing is to spin the magnetic fields relative to the sample in a certain way, which has apparently been demonstrated only for a sample inside the coils.

(7) Early experimental efforts have shown that NMR signals from protons in water are weak and difficult to detect, using their precession in the earth's magnetic field. A laboratory free of iron objects is required. Signal-to-noise ratios are marginal unless frequency filtering, coil design, the prepolarizing field and its turn-off process are optimized. Signals from solids, especially from external samples, are inherently weaker and shorter in duration. However, by employing much stronger precession fields and the Swiss pulse-echo techniques, success in detecting NMR signals from suitable solid minerals around a borehole, for assay logging, should be feasible. EPR logging has already been demonstrated by Chevron Research Co., but its applicability to assaying solid minerals would require further research to determine.

1.3 CONCEPTUAL DESIGN OF AN ASSAY-LOGGING SYSTEM

Figure 1 is a block diagram of an NMR assay logging system conceived as a result of this research. The plastic-jacketed logging sonde contains an array of transverse field-generating coils operating at 100 to 500 amperes dc, switched on and off by SCR circuits controlled from the surface, and a power supply to supply this current. It is filled with oil for cooling and pressure resistance. The sonde also contains a hum-bucking arrangement of transverse signal-pickup coils at right angles to the field coils, which feed a preamplifier gated on and off by the surface equipment. All coils employ powdered-iron cores for improved coupling to the external rock, with good high-frequency response.

The surface equipment includes an ac power source, a programmer to control the preamplifier and current-switching control in the sonde, a solid-state data storage and accumulation device, and an oscilloscope or other means of display.

The operating cycle includes the following steps:

(a) The field coils are turned on for 1 second (or longer, as required by a particular mineral) to prepolarize the nuclei of interest in the zone of investigation, at a field strength of 100 gauss or more.

(b) The field is reduced to 2 gauss in a time of 10 to 50 microseconds, and is then collapsed to zero in 1 or 2 microseconds.

(c) The nuclei of interest then precess as a coherent group about the earth's magnetic field. When they have turned about 90° (that is, after a precalculated time of the order of 20 microseconds), the field is

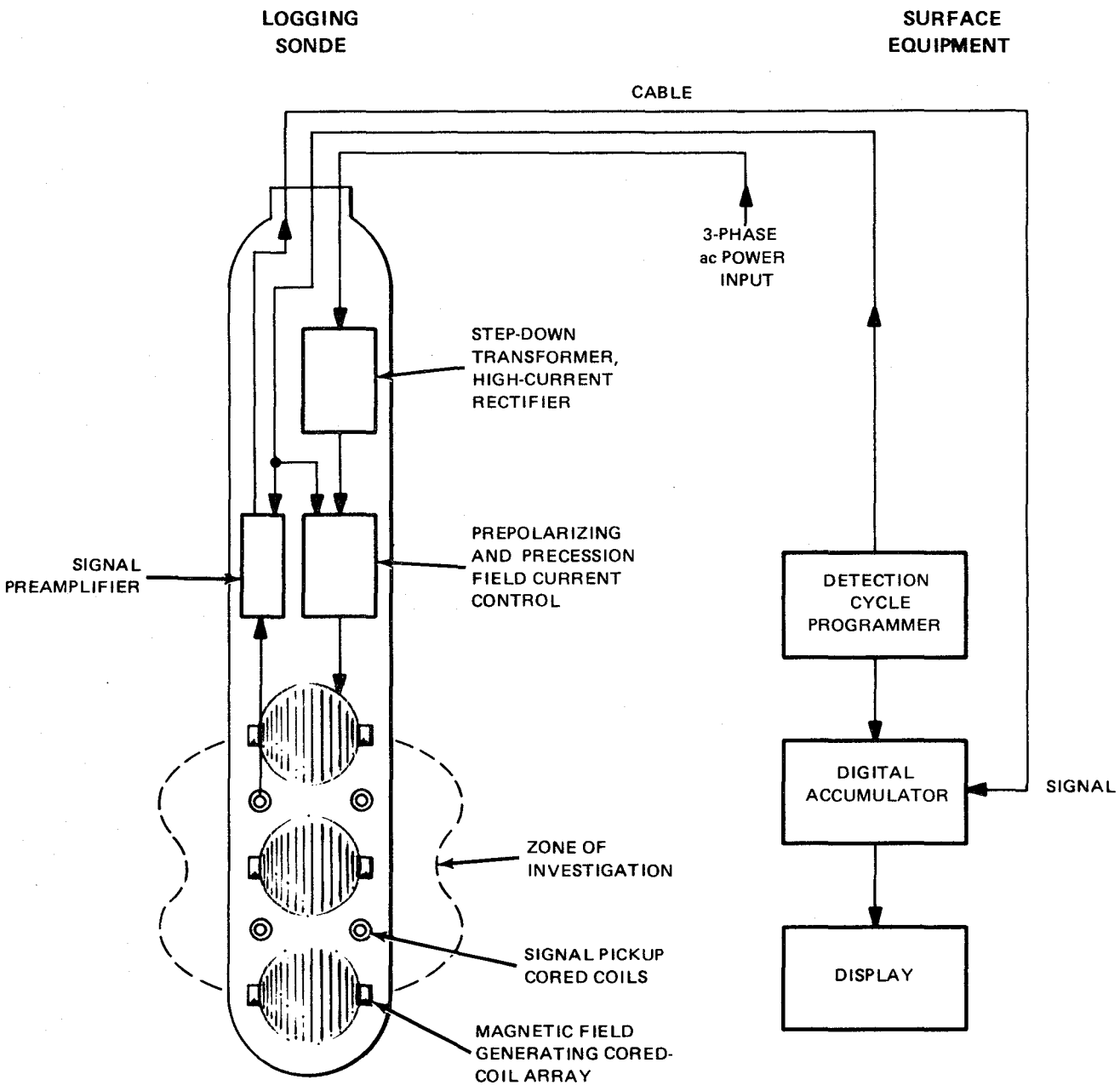

Figure 1. Concept of NMR assay logging system

restarted by a high-voltage capacitor discharge, and is rapidly restored to an intermediate value H_1.

(d) The nuclei of interest precess about the restored field H_1 at an average frequency $f = \gamma H_1/2\pi$ where H_1 is the average field strength in the zone of investigation and γ is the gyromagnetic ratio of the nuclei of interest. For H_1 = 100 gauss, f = 400 kHz for fluorine. The preamplifier is turned on briefly to detect the signal which is stored in the accumulator on the surface.

(e) Because of the inhomogeniety of H_1 in the zone of investigation, the group of precessing nuclei quickly gets out of phase and the signal vanishes. The field H_1 is then reversed within 20 microseconds or less. The nuclei precess backward and again come into phase, giving a pulse echo which is amplified and stored.

(f) Process (e) is repeated until coherence is finally lost because of spin-spin coupling effects. This may occur in 100 microseconds or so following step (b), depending on the mineral of interest.

In this sequence, steps (c) through (f) may be accomplished by applying a powerful alternating current at a frequency of 30 kHz or so to the field coils, perhaps resonating them with a capacitor for this purpose. The field must begin suddenly (within 5 microseconds?) at a current peak to achieve proper phasing. The signal-echo bursts will appear in the pickup coils at the times of peaks and troughs of the high-current waveform.

There are additional variations of this basic scheme, based on the publications of the Swiss, that might improve it. One might be the application of a resonant forcing field by means of one of the coil sets (or a third, axial solenoid) at some time during the cycle, to prolong the signal-train duration by improvement of the coherence of the group of nuclei.

1.4 RECOMMENDATIONS FOR FURTHER RESEARCH

The NMR logging system described in section 1.3, above, and possible variants and improvements thereof, should be developed into a practical working tool. Beneficiaries would be the large and important U. S. phosphate-mining industry, and to a lesser extent, exploration efforts for fluorspar and bauxite in this country. In future, oil-shale assaying and grading would also benefit.

In addition, we recommend continued research on mining applications of EMR techniques in the following areas:

(a) A comprehensive experimental study of the EPR signatures of numerous valuable minerals and natural U. S. ores thereof, to determine whether these spectra can be used to identify and quantify such minerals in such ores. In conjunction, further information should be obtained on the general availability of the patented Chevron EPR logging equipment, and its technical limitations.

(b) Study of the feasibility of employing the ENDOR (electron-nuclear double resonance) process on at least some impure solids at room temperature, to identify nuclei of the many valuable elements which produce weak NMR signals or which occur at low concentrations in important U. S. ores. Some examples are copper, molybdenum, zinc, lead, silver, vanadium and uranium.

(c) Extension of the work of this program to experiments on the NMR effects of additional ores of the commercial metals, of potassium and sodium minerals, and possibly hydrocarbons. Continuation of experimental studies designed to improve the sensitivity of NMR logging and surface-assay equipment; this would include further magnet and field-switching experiments, tests on multiple-pulse and rotating-field techniques for spectral line-narrowing, and further investigation of the unpublished achievements of the petroleum industry in NMR logging.

2. THE GATHERING OF BACKGROUND INFORMATION

In embarking upon any study program in applied science, it is necessary to find out what others have already done. There is fortunately a voluminous published literature on the EMR arts to refer to, and there are many practicing specialists to consult. We knew that most of the work would be extraneous to our objectives, so we must be very selective. The process of literature searching and study we followed, as well as its results, supplemented by visits and consultations, are detailed in this section of the report.

2.1 LITERATURE SEARCHES

The primary literature search for "indicator minerals" included five searches "by hand" of various indexes plus six automatic searches of the large on-line data bases in the Lockheed computer in California. All work was done at the Science Library of Southern Methodist University, Dallas, using a remote terminal unit.

The major automatic searches were performed on Physics Abstracts back to 1970, Chemical Abstracts back to 1972, and the NTIS government reports back to 1964; only the recent years were available in the disc memory. As descriptors, the names of 46 specific ore and rock-forming minerals, plus the words "ore", "mineral", and others were used in conjunction with 24 words and acronyms for particular kinds of resonance. By examination of the resulting printouts of several hundred abstracts, the extraneous material was reduced further. Finally, the papers themselves were located in the files at SMU.

2.2 COMMENTS REGARDING THE LITERATURE SEARCHES

(1) Approximately 315 papers, patents and reports (including a few duplications) were selected from all the world's literature, from the beginnings of NMR up to the present. These have been selected from a total of more than 3 million technical articles and other items published during the past 20 years. Coverage is considered to be very thorough from 1970 to September 1976, and reasonably complete before 1970. These searches have not purposely included techniques, equipment or magnets to any degree. Separate, shorter searches on these subjects, concentrated on recent work, were performed.

(2) Our objective in performing these searches has been to locate information already obtained by others, telling which commercial ore minerals have been shown to exhibit EM resonances that may be specific indicators of those minerals. Equally important has been to find out how such resonances were obtained, and the frequency vs biasing field, linewidth and other

parameters of such resonances. It was found that EPR (ESR) resonances are less specific and diagnostic of composition than NMR and NQR, since the former are produced by trace impurities*, and the latter by major constituent elements. Since NQR signals tend to be relatively weak, major emphasis was placed on NMR spectra and techniques. As a rule, only literature dealing with solids was considered.

(3) The principal difficulty in selecting useful references from the large number available has been to reject the majority on NMR, etc., which deal with liquids, with organic compounds or with synthetic "minerals" especially prepared for research in masers, lasers, semiconductors, fluorescent, magnetic and electrostrictive materials, or for the study of crystallography and the basic resonance phenomena themselves. Such synthetics include many special fluorites, tungstates, rutiles, corundums, garnets, ferrites, and zeolites of high purity not found in nature. Many contain rare-earth metals as a major constituent or a dopant, or they are prepared as single crystals or thin films. Many papers were rejected because all the experimental data had been obtained at temperatures near absolute zero, where the spectra tend to be very different from those taken near room temperature.

(4) The selected papers and reports were published in many languages. English and Russian seem to be about equally prevalent, with most data on natural minerals in Russian. There are also many papers in German and French. There are a few in Japanese, Chinese, Polish, Ukranian, Hungarian, Italian, and Spanish. Most of these have English abstracts; most of the Russian papers have also been translated into English.

It was possible to read all the papers in Western languages, and to evaluate most of the others by means of the titles, abstracts and illustrations. A few in unusual languages were found to merit commercial translation.

(5) Key papers were found which promised feasibility for assaying by NMR, etc., of the following:

(a) Fluorine content of fluorite concentrates.

(b) Phosphorus content of apatite concentrates and in "rock phosphate."

(c) Oil yield of oil shales.

(d) Permeability of various rocks.

Very little was found on the sulfides and carbonates of copper, lead and zinc.

*An excellent summary article on EPR in minerals by A. S. Marfunin at the USSR Institute of Ore Deposit Geology, Petrography, Mineralogy, and Geochemistry has been published in French. (See bibliography.) It states that all natural minerals contain impurities, which give EPR spectra and show only the crystallographic details and geologic history of the mineral.

(6) Most reports on EMR of natural minerals are confined to work with samples from particular deposits, mostly in the USSR. Practically no work of this sort had been performed on U. S. ores.

(7) Study of the initial group of publications inevitably led to additional important references. The literature searches and study, therefore, continued sporadically throughout the entire program.

2.3 SOME POSITIVE RESULTS FROM THE LITERATURE

The papers which have been especially encouraging include the following:

(1) "Radiospectroscopy of Minerals," by A. S. Marfunin, Geol. Jour., v. 4 pt. e, (1965), p. 361-390. This translation from the Russian is a simple, readable summary of the field of EMR in minerals as of 1965, by the world's leading authority. It contains a large bibliography. He shows that ESR signals come only from the minor constituents of minerals, which of course have little or no value in identifying commercial amounts of valuable elements or minerals. NMR signals in minerals have spectral lines 1000 times as broad as in liquids, which however can be narrowed by spinning the sample at 20-60 kHz about an axis tilted 54°44' from the steady magnetic field (the "magic angle"), or by rotating the rf field. Only ten elements had been observed in minerals by NMR, of which the proton (hydrogen) is most prominent. Others are Li, B, Be, Na, Al, As, Sb, Bi, and Cu. Pulse methods are favored because initial signal amplitudes do not depend on line widths.

(2) "NMR Study of the Electronic Structure of Solid and Liquid Silver Metal," by D. Zamir, Phys. Rev. B, v. 10, No. 6 (1974), p. 2343a. Native silver would be harder to detect by NMR than is copper but is easier than native gold. A special, low-frequency pulsed spectrometer was used with large magnets. At room temperature, T_1 was 0.03 sec. and T_2 was 0.008 sec.

(3) "Feuchtemessung mit Hilfe der Magnetischen Kernresonanz," by W. V. Bette and H. Winterhoff, Feinwerktechnik & Messtechnik, v. 83, (1975), part 5, p. 218-224 (in German). Describes successful NMR measurement of moisture content and combined-hydrogen simultaneously, in solids: three commercial organic products and one mineral. After calibration with a particular substance, the equipment can operate automatically and continuously on a process stream of material, as in a factory.

(4) "Magnetische Kernresonanz von Titan in Rutil mit Hilfe von dynamische Kernpolarisation," by Ch. Gabathuler and E. E. Hundt, Helv. Physica Acta, v. 44, (1971), p. 558-559. Reports that the titanium in natural rutile has yielded an NMR signal and its quadrupolar constants for the first time, because a pulsed technique greatly enhanced the sensitivity of the experiment.

(5) "Using Broad-Line NMR Spectrometry to Estimate Potential Oil Yields from Oil Shales," by A. W. Decora, F. R. McDonald, and G. L. Cook, U. S. Bureau of Mines Report of Investigations 7523, (1971). This work, done at the Laramie Energy Research Center, showed an excellent correlation between the strength of the proton NMR signal for numerous (dried) samples of five different oil shales, and the results of Fischer analysis for oil yield. It appears that this work could be applied directly to NMR logging assays of oil shale in drill holes. It is very encouraging.

(6) "NMR Studies of Hydrated Sodium Tetraborate Minerals" by J. D. Cuthbert and H. E. Patch, Can. Jour. Phys., v. 33, No. 156 (1955), p. 1912. The NMR signals and quadrupole coupling constants were determined at room temperature on 3 ml. single-crystal samples of three important ore minerals of boron: kernite, borax and tincalconite. The zero-field NQR responses are all between 478 and 3,588 kHz, which is fairly encouraging.

(7) "Assay of Phosphorus in Rock Phosphate" by G. Datta, B. K. Banerjee and P. K. Ghosh, Technology (India), v. 10 #12, (1973), p. 66-68. This paper is most applicable to our problem, of 4 papers found on industrial application of NMR for phosphorus assay (one Indian, one German, two Russian). The authors say that their natural phosphorus ores are already doped with sufficient paramagnetic ions to give short relaxation times and permit rapid runs. They obtained an excellent correlation of NMR assays with chemical assays for phosphorus, on samples ranging from 2.5 to 42% phosphorus content.

(8) "Spectres de Haute Resolution dans le Champ Magnetique Terrestre," by George J. Béné, Rev. Roumaine Phys. (Romania), v. 15, No. 8, (1970, p. 891-910 (in French). This was the single most exciting publication found. Béné and his students (at the Institute for the Physics of Condensed Matter in the University of Geneva, Switzerland) have written many papers on low-field and earths-field NMR techniques. Several techniques are proposed and some are demonstrated, starting with the simple method of Packard and Varian [Phys. Rev., v. 93 (1954), p. 941] wherein a strong prepolarizing field is applied to a large sample of water for time T_1, then is suddenly cut off so that the aligned protons precess about the earth's field. This technique is the basis of all proton magnetometers, as well as most NMR well-logging.

Béné has also demonstrated a more sensitive technique, which does not require uniform magnetic fields! Two crossed coils surround the sample. The procedure is as follows:

(a) A strong polarizing field Hp(150 gauss) is applied to the sample for a time long compared to T_1, the spin-lattice relaxation time of the sample nuclei. It is then suddenly cut off (within 1 or 2 milliseconds).

(b) The nuclei then precess about a smaller, perpendicular field H_1 (15 gauss) which has already been established. Since this field is not homogenous, they quickly get out of phase and the Larmor oscillations induced in the Hp coil vanish.

(c) After a time t short compared to T_1 and T_2 for the sample nuclei, field H_1 is reversed. The nuclei then precess in the opposite direction and come back in phase after another time t, because the spatial distribution of the reversed field $-H_1$ is identical to that of the forward field H_1.

(d) The field H_1 may then be reversed again periodically (e.g., each 0.2 second) giving a series of signals which decay in amplitude in a time proportional to T_1. Such a signal train is shown in figure 2.

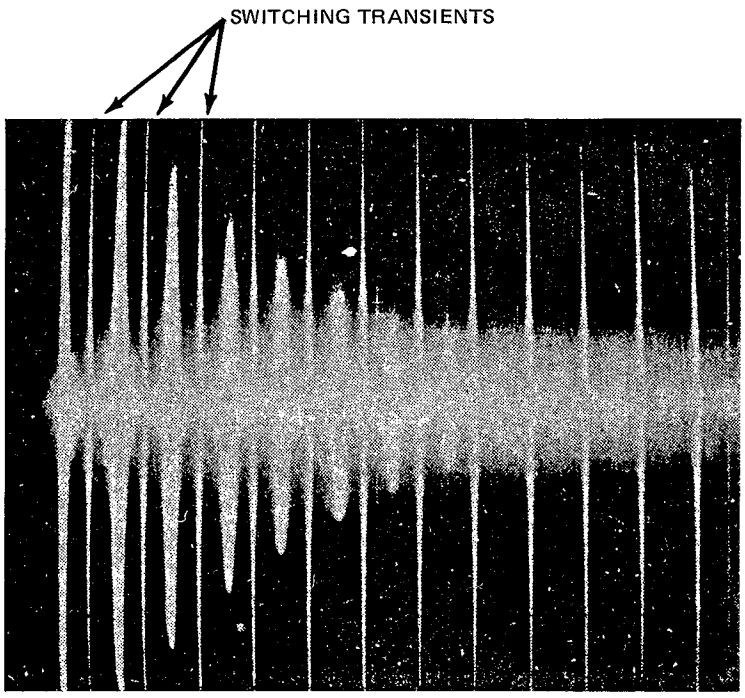

Figure 2. NMR signals using Béné's reversing - field method

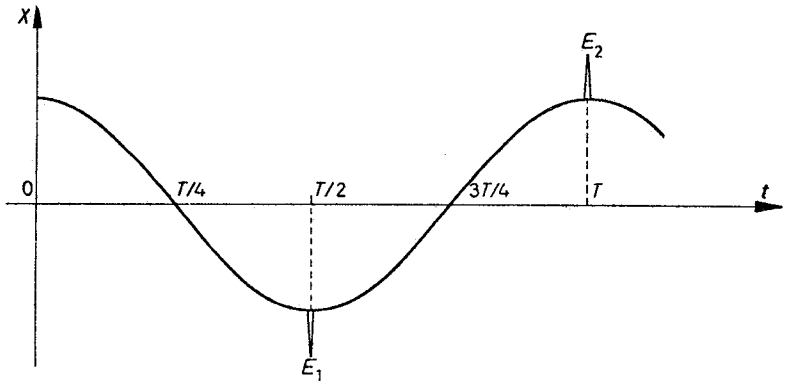

Figure 3. Spin echoes in an alternating transverse field (after Béné)

This technique, and others related to it which employ field-reversal, appear to be ideal for borehole NMR assaying; the inhomogenous fields in the rock outside of the coil system can be used, and the volume sampled can be very large, comprising most of the rock mass within the strongest part of the field, that is, a cylinder about 1.5 L in length and L in radius, where L is the length of the coils. The signal strength should be proportional to L^2, and also to H_p and H_1, all of which are within our control.

2.4 FURTHER INVESTIGATIONS OF THE SWISS TECHNIQUES

Nine papers in French and five in English by G. Béné, B. Borchard, E. Hiltbrand, R. Séchehaye and others (at the University of Geneva, Switzerland) on low-field NMR have been located and reviewed. The material covered by several of them is much the same, but a number of novel ideas are proposed for the use of the earth's field, other weak fields, and inhomogeneous fields for NMR. The use of a secondary dc field, which is periodically reversed, was mentioned above.

An easier scheme to implement is well-explained in two papers*, but has never been tried anywhere. This scheme is illustrated in figure 3. At time zero, the strong prepolarizing field H_0, along the z-axis say, is suddenly switched off, and a secondary field H_1 along the the x-axis is turned on. (We think it may be possible to transfer half of the magnetic energy from one coil to the other very quickly.) The nuclei aligned with H_0 begin to precess about H_1, but quickly become dephased because of field inhomogeniety. However, field H_1 is a sinusoidally alternating field; the second quarter-cycle refocusses the nuclei, producing pulse-echoes E in the H_0 coil at time T/2, again at T, at 3 T/2, etc. The beauty of this scheme is that it eliminates all switching events and transients except the first. The sinusoidal waveform must be highly symmetrical, i.e., there cannot be any odd harmonics present. It may also be necessary that the period T be less than the minimum nuclear randomizing time (spin-spin decay time T_2), which is apparently only 18 microseconds for fluorite and 200 microseconds for two phosphate ores (see section 2 of this report).

*G. J. Béné, "NMR at Zero Frequency," Proc. 16th Ampere Congress, 1970, Bucharest, p. 15-33.

*G. J. Béné, "New Spin Echo Techniques in the Earth's Magnetic Field Range," Chim. Pur. et Appliq., v. 32, 1972, p. 67-77.

Béné calls attention to another phenomenon which may provide a basis for a method especially good for solids, where T_2 is short but T_1 is long. This is the use of the switching transients in a square-wave reversing field H_1 to excite spin "echoes." Béné's explanation is that strong switching transients contain Fourier components of the frequency at which the nuclei resonate in field H_1, so that this technique somewhat resembles the conventional strong-field method employing resonant RF pulses. It should be relatively easy to implement, however, and should still operate with relatively weak, inhomogeneous fields. Figure 4 is a demonstration of this method given by Béné. The "echoes" are unsymmetrical. The rising portion "is governed by the amplitude of the frequency component involved" (which might be tailored to optimum by shaping the current transient). The falling portion is governed by de-phasing effects, either the inhomogeniety of the field H_1, or the spin-spin relaxation time T_2. The "echoes" diminish with time at a rate governed by T_1, which tends to be of the order of seconds in solids. Apparently, each transient re-aligns the nuclei from their randomness, since each nucleus tends to act as a bandpass filter sensitive only to the frequency component appropriate to the magnetic field strength in its particular vicinity. The scheme deals simultaneously with the problems of wide line widths and short T_2's typical of solids.

Béné, et al, have recently suggested* the enhancement of NMR signals in weak fields by use of the Oberhauser effect. Electronic (EPR?) transitions in a free radical (tanone) have apparently been excited in the earth's magnetic field, at room temperature, by means of a secondary 67 MHz field. This magnetic ordering of the electrons can evidently enhance that of protons in the same sample, because of strong electron-proton magnetic coupling. The experiment is not described in detail, but several references are given which have not yet been followed up. In any event, this suggests that the paramagnetic ions (generally Mn^{+2} or Fe^{+3}) present in most minerals might be used to enhance the weak NMR signals from elements of interest, even at low concentrations. This is an encouraging possibility for future research.

On the advice of several magnetic-resonance specialists, the Principal Investigator attended this conference, which was held in Banff, Alberta during May 1977. About 300 of the pioneers and leading workers in NMR and EPR worldwide were there, and every possible opportunity was taken to discuss our problems with these scientists, as well as to attend pertinent lectures and to examine the latest equipment and textbooks on display.

A principal goal was to meet and talk with Professor G. J. Béné with whom a lively bilingual correspondence had developed concerning his work during the past decade on weak-field and inhomogeneous-field NMR. In the course of our discussions, Dr. Béné provided copies of several new papers on these matters.

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*G. J. Béné et al, "Effect of a Non-resonant Electromagnetic Field on the Frequencies of a Nuclear Magnetic Moment System," submitted for publication in Physical Reality and Mathematical Description, Reidel, Dordrecht, Holland (1974, p. 541?).

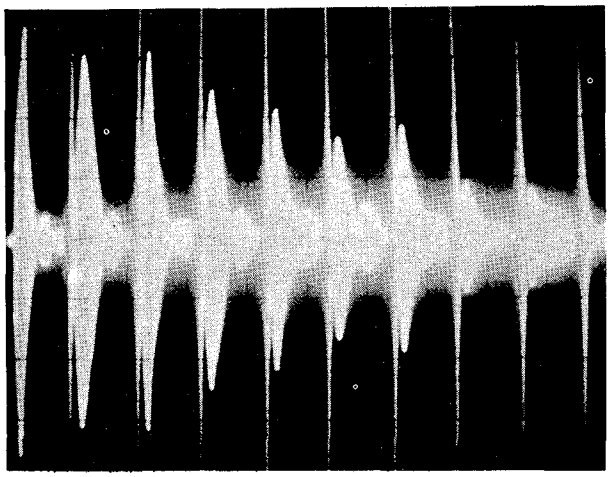

Figure 4. Pseudo echoes from switching transients in a weak transverse field (after Béné)

His group is still active in developing and applying low-field techniques, especially to the problem of diagnosing cancer by exploration through the surface of the human body with external coils. This somewhat resembles our problem of exploring mineral masses external to our coils. Unfortunately, Dr. Béné has done no work with solids, and his techniques have been used only on the proton (hydrogen) constituent of liquids. In his opinion, solids cannot be detected by NMR in the earth's field, because of the great line-width. However, they might be detected by using an auxiliary field H_1 of perhaps 20 gauss; the field-reversing transients must then be perfectly symmetrical to avoid dephasing of different nuclei, which is a cumulative effect. The use of the pure sinusoidal H_1 suggested in several of Béné's papers has never been tried. He expects that the necessary electronic techniques will be very difficult to work out.

Subsequently, in the course of other business in Europe, the Principal Investigator was able to make a side trip to Geneva, Switzerland, to meet with Prof. Béné and his younger colleagues, Dr. Bernard Borchard and Dr. E. Hiltbrand, and to see and discuss their equipment. It was also possible to obtain three recent theses and a few new papers in the field, particularly one describing related work in Poland.

All the current research by the Swiss group is devoted to measuring the decay times T_1 and T_2 of protons in biological liquids, either *in vitro* or *in vivo*. Measurements in the living human body require the special techniques they use. All their work at this time is done with a single prepolarizing and signal-pickup coil (said to be easier than the two-coil methods), with precession about the earth's field. The aim is to distinguish normal from pathological tissues on the basis of differences in T_1 and T_2, since all their financial support now comes from cancer research organizations.

A few years ago, they were asked to apply their techniques to oil-well logging by a French company (possibly Schlumberger). Apparently the supporting funds for the Jussy laboratory were cut off when their first attempts failed, and the required refinements were never arrived at under the commercial sponsorship.

The Jussy laboratory has been in operation about 22 years. There has been a steady outflow of publications into the permanent literature. We are now in a position to extend the Swiss techniques in the direction of solid-mineral assay logging.

2.5 MISCELLANEOUS PROGRAM STUDIES

2.5.1 Review of Basic or Historic Papers

As the literature study proceeded, the need was felt to review several older papers explaining particular phenomena in EMR, which are of possible value to this program.

Ten basic papers in the physics literature, announcing or describing major advances in NMR technique for solids, were carefully reviewed. Another ten were examined in a cursory manner, and a dozen more were put aside for possible future study. Many such papers are highly theoretical and require considerable time to digest.

The most important ideas reviewed for possible application to our problem have to do with the development of pulsed - RF spin-decay and spin-echo methods, and with line-narrowing in solids. The following papers are admirable examples of the first group:

H. C. Torrey, "Transient Nutations in Nuclear Magnetic Resonance," Phys. Rev., v. 76, p. 1059 - (1949).

E. L. Hahn, "Spin Echoes," Phys. Rev., v. 80, p. 580-594 (1950).

H. V. Carr and E. M. Purcell, "Effects of Diffusion on Free Precession in NMR Experiments," Phys. Rev., v. 94, p. 630 - (1964).

I. Solomon, "Rotary Spin Echoes," Phys. Rev. Lett., v. 2, p. 301-302 (1959).

The second group, dealing with narrowing of resonance lines in solids, included the following:

E. R. Andrew and R. G. Eades, "Possibilities for High-resolution NMR Spectra of Crystals," Disc. Faraday Soc., No. 34, p. 38-42 (1962). (Gives the theory for the technique of rapidly rotating the sample about an axis inclined 54°44' to the aligning field, the "magic angle," to remove dipolar broadening. Also mentions electrical rotation of the field about a fixed sample by means of a 3-coil system.)

S. S. Jha, "Narrowing of NMR Resonance Lines in a Double Frequency R. F. Field," Jour. Phys. Soc. Jap., v. 21, p. 42-48 (1966). (Gives the theory for line-narrowing using two frequencies. Solids require RF fields above 100 gauss, unfortunately.)

P. Mansfield and D. Ware, "Nuclear Resonance Line Narrowing in Solids by Repeated Short-pulse R. F. Radiation," Phys. Lett., v. 22, p. 133-135 (1966).

J. S. Waugh et al, "Approach to High Resolution NMR in Solids," Phys. Rev. Lett., v. 20, p. 180-182 (1968). (Both these papers show experiments in which fluorite lines were narrowed by factors up to 10,000 by application of a sequence of very strong RF pulses.)

2.5.2 Magnetometer Publications

Prof. Béné's papers refer frequently to two short American papers[1,2] by members of the Varian Corporation, implying that these pioneered the use of the earth's field and a prepolarizing field in proton magnetometers. These "papers" describe briefly both the use of a prepolarizing field to obtain a resonant decay signal in the earth's field, and the use of a short dc pulse later on to produce a spin echo for the measurement of T_2 despite an inhomogeneous earth's field.

To assist in our own experiments (see part 5), and in order to understand better, the existing techniques for NMR in the earth's field, several other publications on proton precession magnetometers were studied. The most important of these made the following new points:

(1) If the prepolarizing field is removed non-instantaneously, the protons tend to follow the resultant field. The critical interval occurs when the polarizing field has diminished to the order of the earth's field.

Overshoot or oscillations then may perturb the proton orbits so as to reduce the signal by a factor of 60 for certain coil orientations[3]. To prevent this, the polarizing field must pass through the critical region in a time much less than one Larmor cycle, and the coil must also have a natural frequency above 8 kHz.

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[1] M. Packard and R. Varian, "Free Nuclear Induction in the Earth's Magnetic Field," Phys. Rev., v. 93, p. 941 (1954).

[2] A. Arnold and D. Mansir, "Measurement of Nuclear Induction Relaxation Times in Weak Magnetic Fields," Phys. Rev., v. 93, p. 941 (1954).

[3] E. Bullard et al, "Curious Behavior of a Proton Magnetometer," Proc. Camb. Phil. Soc., v. 60, p. 287 (1964).

(2) Different coil designs[4] differ in their signal output by a factor of 200. An optimum coil design combines high Q with good coupling to the sample and the generation of a strong polarizing field without overheating. The best shape is a multi-layer solenoid about 1-1/2 times as long as its diameter[5]. Stranded (litz?) wire can improve the signal[6] by a factor of 3 or 4. The use of a toroidal coil, or two solenoids side by side in a humbucking arrangement[6] helps cancel out external interference.

2.5.3 Well Logging NMR Patents

All the U. S. and Canadian patents found (five of each) on NMR well logging were carefully reviewed. All were aimed mainly toward distinguishing oil from water in the medium surrounding the logging tool, by means of the differences in proton relaxation times T_1 and T_2 that are generally found between them. All employ the geomagnetic field in some way. Many innovations of possible value to our program are published in these patents, including the following:

(1) Elongated rectangular coils, similar to our "transverse" coils, for good coupling to the external medium. These are claimed in such a general way in Chevron's Canadian patent 833135 (and presumably in a related U. S. patent) that a license will be required to use them extensively in well logging. However, we believe there are good alternative techniques not covered by this patent.

(2) Spherical cores in the coils, of a high-frequency material, said to increase the coupling greatly.

(3) Dropping the prepolarizing field first to about 0.5 to 5 gauss, either suddenly or adiabatically, preparatory to fast cutoff through the critical, low-field region. (This technique was also developed and published in 1969 by a Polish group who visited the Jussy lab before us.)

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[4] J. C. Mudie, "An Appreciation of the Design Factors of Proton Magnetometer Sensing Heads," MPL Tech. Memo 157, Scripps Institute, 1 March 1965.

[5] G. Faini and O. Svelto, "Signal-to-Noise Considerations in a Nuclear Magnetometer," Nuovo Cimento, v. 22, series 10, p. 55-56 (1962).

[6] M. E. Berry and T. R. Tullsen, U. S. Patent No. 3,886,440 (1975).

(4) Applying an AC forcing field at f_o, the Larmor frequency of protons in the earth's field, to rephase or realign the ensemble of protons and produce a pulse-echo (Chevron's Canadian patent 863453) or to allow slow termination of the prepolarizing field (Texaco's U. S. patent 3,667,035).

(5) Reapplying the prepolarizing field H_p after an interval, to produce a pulse-echo (Chevron's U. S. patent 3,226,632).

In effect, it uses the earth's field to get a 90° rotation, a method we had recently invented also. There is no indication whether this scheme was actually reduced to practice by Chevron.

(6) Use of a swept CW spectrometer with a large permanent magnet and field-shaping (Texaco's Canadian patent 914758) and advanced signal-detection circuits. The volume sampled is of course very small.

In addition, these patents teach the use of many tricks and ideas already in the public domain. These include the use of silicon controlled rectifiers for switching large currents fast, and the use of balanced hybrid transformers (telephone-type) to obtain 2-way communication over a 2-conductor logging cable. The patents also give a few values of field strength, current, switching time, and other parameters that these practitioners have found appropriate in their experiments, which we may do well to imitate. Study of these patents, while tedious, has been very worthwhile in preparing us to extend the art to solid minerals.

Some of the logging schemes proposed in these patents appear very promising as alternatives to the Swiss methods, especially item (4) above, which is said to improve the signal strength greatly.

It is not known whether these patented methods are better or worse than the Swiss methods. Presumably all, except (6) above, are capable of producing an NMR signal from a substantial volume of material outside of the coils, that is, using weak, inhomogeneous magnetic fields. All except 6 above, require rapid switching of the strongest fields obtainable. However, the Swiss techniques may be preferable because they are not proprietary, having already been published for more than one year.

In their Specifications, the patentees appear to speak from considerable experience in the laboratory. They have evidently spent a great deal of time and funds achieving good signal strength. The Slichter/Texaco patent even mentions possible applications in assaying fluorite, phosphates, and spodumene (the same minerals we chose by an independent process---see part 3)! If the ideas in these patents are used in solid minerals assay logging, it will be advisable to work closely with the oil companies, perhaps under license, even though this might not be legally necessary because of the limited combinations covered in the patent claims.

2.5.4 Publications on Fluid Permeability

The Technical Project Officer had expressed interest in EMR logging techniques for the measurement of the permeability of rocks to liquids, and forwarded a reprint published in 1966 on this subject. This paper, by Delmar O. Seevers of Chevron Research Company, is entitled "A Nuclear Magnetic Method for Determining the Permeability of Sandstones." The principle employed is that proton relaxation-times T_1 for distilled water in synthetic and natural sandstones show excellent correlation with permeabilities. However, an empirical proportionality constant, different for each well, must be inserted.

Further study of this subject was begun by phoning Dr. Seevers (see section 2.6.5) and by combing through the tables of contents of the entire set (through 1976) of the Proceedings of the annual logging symposia of the SPWLA (Society of Professional Well Log Analysts) at two local libraries. From these Proceedings, all papers dealing with NMR logging were photo-copied, and all papers dealing explicity with the measurement of fluid permeability were examined. Six major papers were copied in full, of which three (all by A. Timur of Chevron) were published later than the 1966 paper by Seevers, as follows:

"Effective Porosity and Permeability of Sandstones Investigated through NMR Principles" - 1968.

"Analysis of Sidewall Samples by NMR Methods" - 1971.

"NMR Study of Carbonate Rocks" - 1972.

The three papers published in 1960 and 1962 were by various authors at several different companies, especially the Byron Jackson Co. (Borg Warner), and Shell Development. None of these companies seem to have published in the SPWLA Symposium Proceedings since 1962. In the references of this group of papers, several important earlier papers are cited. These were not located.

All these papers were studied briefly. Some of the ideas to be found in them include the following:

(a) The free fluid index (FFI) is given by the amplitude of the NMR signal, and can be another measure of formation porosity.

(b) The relaxation curve (amplitude vs time after a pulse) may exhibit two different decay times. The short T_1 was once attributed to water and the long T_1 to oil. Things are probably not that simple.

(c) The borehole fluid must be preconditioned by adding magnetite to quench its NMR very quickly. If the T_1 of its filtrate is made very different from that of formation water, invasion can be estimated by NMR, just as has been done by resistivity and neutron (boron) methods in the past.

(d) Success in measuring permeability apparently varies with rock type. Considerable empirical research has to be done to develop necessary techniques, formulas, and constants for each class of rocks.

2.5.5 Consultations by Telephone

To shed light on some of the perplexing questions posed by our experiments and studies, we sought counsel from some of the "senior statesmen" in the NMR field by means of telephone conversations. All were cordial and helpful. Their advice was encouraging.

(1) Dr. Delmar O. Seevers, senior technical consultant with Chevron Research Co., La Habra, California. Our chief objective in calling Dr. Seevers was to learn the present status of NMR logging for fluid permeabilities of rocks. We learned that Chevron has extended Seevers' 1966 work to fine-grained sands and to carbonates. Otherwise, Chevron has turned over all activity to the Schlumberger Well Service Company under a license based on Chevron's basic patent of about 1953. Schlumberger has finally developed what is believed to be a reliable commercial logging instrument, which is now being tested by Chevron. This instrument employs the earth's field and obtains the intensities and relaxation times of the proton signals, for porosities as low as 6%, with a good signal-to-noise ratio. The prepolarizing current of 30 amperes cannot be switched off in less than 5 milliseconds without a voltage breakdown. Their signal decay time is limited by earth's-field inhomogeneities, especially from paramagnetic impurities in the rocks.

There did not appear to be any opportunity or any need for our program to contribute to the permeability-logging art at this time. Ultimately, if a successful technique employing a reversing secondary field and spin-echoes were developed, some improvements might be contributed.

Chevron, Schlumberger and Texaco have all attempted to use a secondary field H_1, to increase the signal strength. All failed, because of field inhomogeneity. However, all were attempting to get pulse decays. Seevers has tried a field-reversing method similar to that of Béné in the lab, with the sample inside of Helmholtz coils. He found that the pulse echoes so produced are much more tolerant of field inhomogeneities than are pulse decays. He encouraged us to try the field-reversal method with external samples (that is, with the sample surrounding the coils). The echo durations may be only a few milliseconds in duration, for protons.

Chevron patented an ESR logging method in about 1964. It employed a long permanent magnet for the steady field, and ordinary radio frequencies. It worked well, and gave lines of 1/2 gauss width from asphaltenes in petroleum. They would be interested in similar work on the kerogen of oil shale, and encouraged us to work on it.

Dr. Seevers suggested that our experimental difficulties (see part 5) arose from distortions of the earth's field near the soil. Chevron had to perform a detailed magnetic survey of their land to find a spot suitable for earth's-field NMR experiments. A nonmagnetic building they erected had steel door hinges at first; this was enough to shorten the decay time of water to 60 milliseconds! Liter-sized samples require better field uniformity than smaller samples. Chevron spent a great deal of time overcoming this problem in the 1950's.

Coil design is critical to good signal strength. Chevron has experimented with coils for 20 years and has prepared many internal reports on the subject. It is doubtful if any of this material could be released. Nevertheless, we would be welcome to visit the Chevron laboratories, examine the equipment, and talk with the employees about details.

(2) Fran Miknis, U. S. ERDA (formerly Bureau of Mines), Laramie, Wyoming. This call was made to Dr. A. W. Decora with regard to continuing work on NMR of oil shale mentioned by Dr. Seevers. Dr. Miknis is now carrying on this work, which is all in strong magnetic fields. The present emphasis is on measuring carbon-13, using the protons in a double-resonance technique to increase the signal. Strong RF pulses are used to saturate ("heat") the protons at room temperature. Dr. Miknis later sent us copies of recent reports on NMR work with oil shale. He is interested in a possible logging tool for solids, and is familiar with the problem of rapid field-quenching in earth's-field NMR. He suggested continued contact and visits for the mutual benefit of both programs.

(3) Professor Robert W. Vaughan, California Institute of Technology, Pasadena. Professor Vaughan is well-known in the art for his work in the narrowing of spectral lines in solids. He was not familiar with Béné's reversing-field technique to obtain spin echoes in an inhomogeneous field, but commented several times that it is "a delightful idea" and might work with solids, at a level of 20 gauss. He warned that dipole-dipole type decay is the strongest relaxation effect in solids, and might give us a window (T_2) only 100 microseconds long, to see the pulse echoes. He indicated that spinning the field slowly might lengthen the decay time T_2, although his discussion of the details was highly technical and will need further clarification. He also mentioned that the paramagnetic impurities do not affect T_2, but only T_1. On the whole he was encouraging.

(4) Professor John S. Waugh, Massachusetts Institute of Technology, Cambridge. Professor Waugh, an experimentalist well-known for his work in NMR line-narrowing by multiple pulse sequences, said that line-narrowing in solids requires pulses of very strong "organizing" fields, to overcome the local broadening fields within the crystal, which are of the order of one to several gauss. Kilowatts of power are usually applied to a 2 ml sample, so megawatts might be required for the liter-sized samples employed by a logging tool. Field strengths of 50 to 100 gauss may be required. Line-narrowing in solids by pulsing may therefore be difficult in a logging tool, but is probably feasible.

Professor Waugh was positive that slow rotation of the sample or fields won't remove the dominant dipole-dipole coupling effect; fast rotation is required, at several thousand revolutions per second. He was surprised at our suggestion that the fields in an external sample might be rotated rapidly by a polyphase arrangement of coils. He mentioned that Professor E. R. Andrew of Nottingham University had done this with an internal sample for EPR, as a novelty about 1970, and had published the result. Professor Waugh invited further conversation and visits to his laboratory, and would like to hear of our progress in applying all the novel techniques we have found to NMR.

3. PRODUCING STRONG AND UNIFORM MAGNETIC FIELDS OUTSIDE OF A BOREHOLE

In this program, we tried to seek anew for techniques of magnetic field generation that would be better than those employed before.

3.1 PRODUCING STRONG MAGNETIC FIELDS

We performed a short study of the technical literature and made several contacts with makers of high-strength magnets. We compared all the available methods of producing strong magnetic fields, as to their effectiveness in producing a strong field in the rock outside a liquid-filled borehole of limited diameter. The main parameter to be compared was considered to be the total available magnetic flux, or its equivalent for very long magnets: (average field strength) x (cross-section), both factors referring to the "active area" at one end of the magnet (that is, the inside of a solenoid, for example).

On this basis, some of the methods used to produce extremely high field strengths (above 50 kG) appear to be unfavorable because the high-field region is very small, and most of the available borehole cross-section must be filled with coils, cooling means, and thermal insulation.

The investigation assumed that the magnet will be configured in the form of a solenoid with a length-to-diameter ratio of between 2 and 10, a diameter of 5 inches (although the entire argument can be scaled down to a diameter of 2 inches), and that the magnet must be operated (power, cooling, etc.), at a depth of up to 1,000 feet.

Three basic approaches have been considered, (a) permanent magnets, (b) high-current air core solenoids, and (c) superconductive solenoids. We have prepared figure 5 to aid in a comparison of power, cooling, and field strength for the three approaches.

(1) Permanent Magnets. Some very significant advantages are associated with the use of permanent magnets:

(a) Lowest cost approach to the problem.

(b) No power required.

(c) No cooling required.

(d) Can be made as long as desired, whereas electromagnet solenoids and superconductive solenoids have power requirements and cooling requirements that are proportional to length. The advantages of a longer solenoid are obvious.

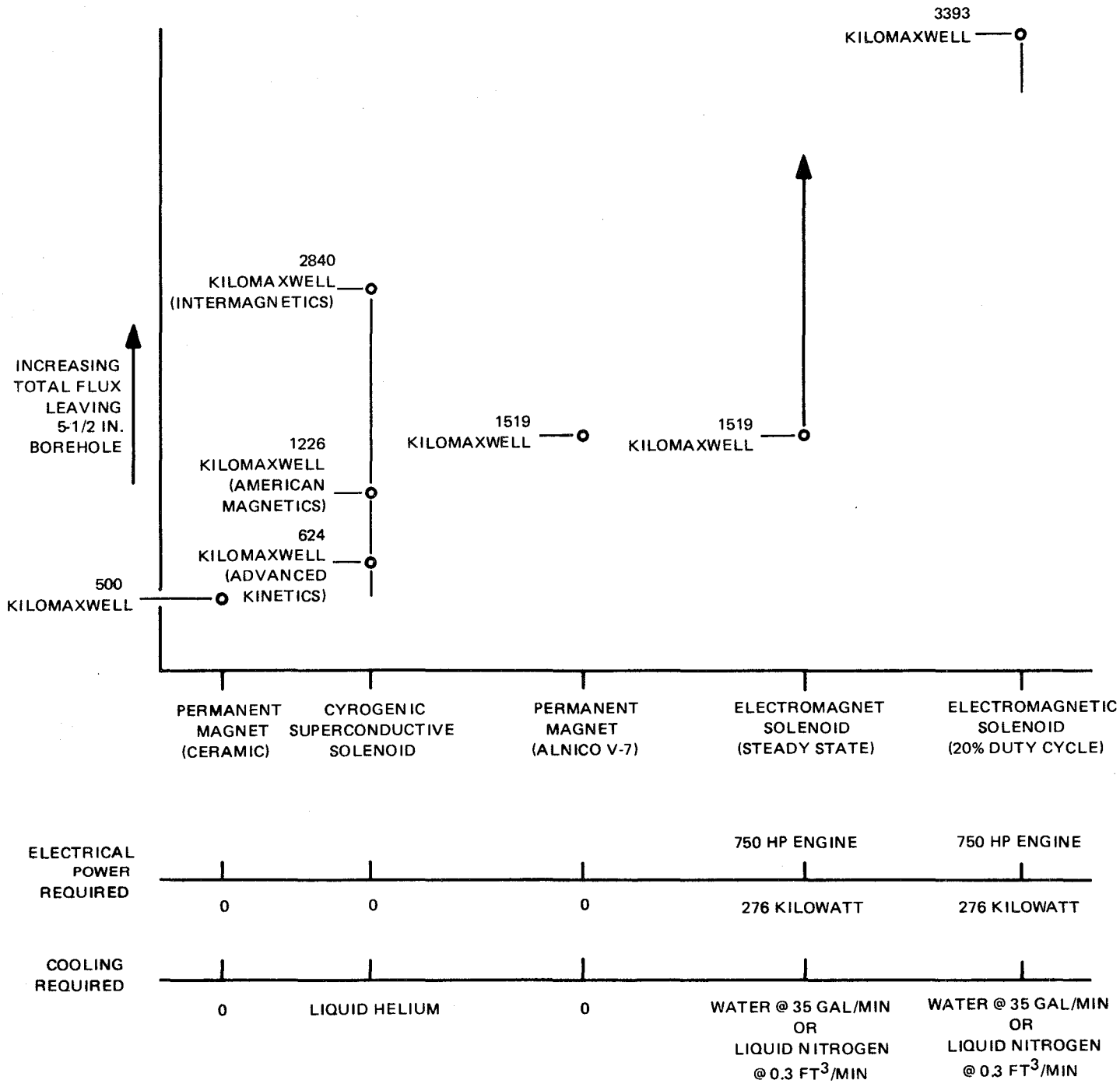

Figure 5. Comparison of power, cooling, and field strength

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(e) The use of a permanent magnet could apparently result in the generation of more magnetic flux in the earth surrounding the borehole than either of the other two methods, if reasonable constraints on power, cooling, and cost are assumed. To equal the flux of the permanent magnet by utilizing an electromagnet solenoid would require a power input of approximately 276 kilowatts per foot, as will be seen from the calculations of sections (a) and (b).

Consider the characteristics of Alnico V-7 as shown in the demagnetization curve* of figure 6. When current in the magnet charger is turned off, the operating point of the magnet drops to an H of zero, as shown by the point B_R on figure 6. When the magnet is removed from the magnet charger it is open-circuited, and a self-imposed demagnetizing force exists which forces the operating point of the magnet to run down the demagnetization curve from B_R, toward H_C, to some intermediate operating point. This point at which the magnet will operate is determined by the permeance coefficient. The permeance coefficient is a function of the length to diameter ratio of the magnet*, as shown by figure 7. It can be seen from figure 6 that the magnet will operate, open circuit, at a point of 12 kilogauss. Since the magnet cross-section is 126 square cm, a total flux of 1520 kilomaxwell will be established through the magnet and through the surrounding earth:

12 kilogauss x 126 cm^2 = 1520 kilomaxwell

The Alnico V-7 would have to be fabricated in 4" long sections, each 5" in diameter. It would weigh 130 pounds and would cost about $2000. That price includes charging the magnet. It can be made with a small hole in the center for assembly and packaging, or, it can simply be enclosed in an aluminum case. A magnet of Alnico V would have about 90% as much B_R but would cost about 35% less than a magnet of Alnico V-7. (The information in this paragraph was supplied by Mr. Jerry Fiepke of Colt Industries, P. O. Box 100, Elizabethtown, KY 42701.)

(2) Electromagnet Solenoid. The advantages of this approach are:

(a) The strength of the field generated is limited only by the amount of available power and cooling capacity.

(b) The field strength for a given power input can be multiplied by using a low-duty-cycle, high-current pulse.

(c) Only by this approach can pulsed fields, for use in the methods of Bené, be generated.

*Indiana Steel, Products Division, 1976, "Design and application of permanent magnets": PM Manual 6A, Valparaiso, Ind.

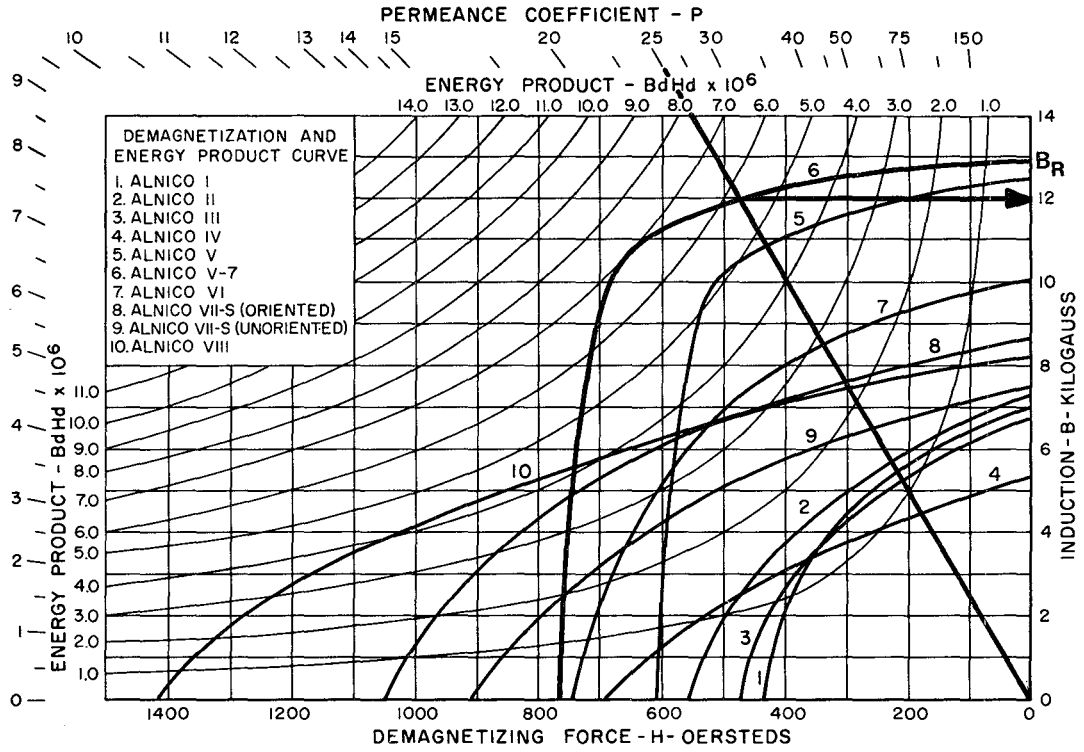

Figure 6. Demagnetization and energy product curves for Cast Alnico magnets (Indiana Steel)

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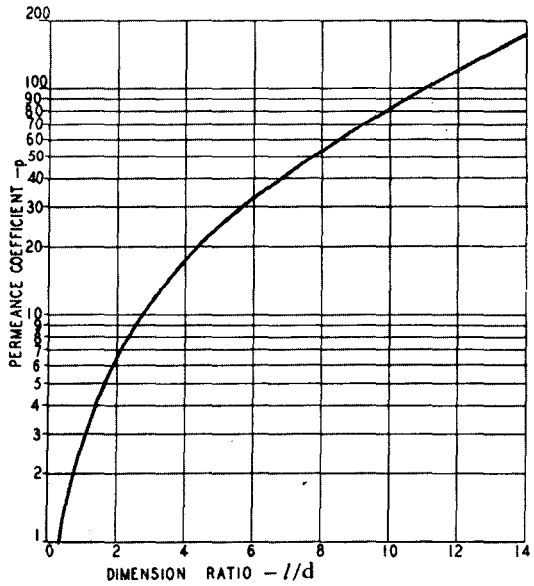

Figure 7. Permeance coefficient vs dimension ratio of bar magnets (Indiana Steel)

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The disadvantages of this approach are:

(a) A large, expensive, motor-generator is required.

(b) It requires the transmission of large currents over distances of up to 1000 feet. The large electrical cables will make for an awkward system, unless high-voltage ac and downhole rectification are used.

(c) An elaborate cooling system may be required - with the attendant complications of such a system.

An equation for the computation of the field within a long solenoid is given by Montgomery* (eqn 1.25, page 7).

$$H_o = G'(\alpha) \frac{(w'\lambda)}{\rho}$$

where: λ = space factor = .8

w' = power per unit length (assume 276 kW/ft = 9.05 kW/cm)

$\alpha = \frac{\text{Solenoid OD}}{\text{Solenoid ID}}$ = 1.25 (if OD = 12.5 cm and ID = 10 cm)

$G'(\alpha)$ = a function of α (from Montgomery page 8, $G'(\alpha)$ is .23 for an α of 1.25)

ρ = resistivity of copper = 1.72×10^{-6} ohm cm

For a 12.5 cm OD, 10 cm ID solenoid with 9.05 kW/cm applied, and cooled to 25°C,

$$H_o = .23 \left(9{,}050 \frac{\text{Volt amp}}{\text{cm}} \times .8 \times \frac{\text{amp}}{1.72 \text{ volt cm} \times 10^{-6}} \right)^{1/2}$$

$$= 14{,}921 \frac{\text{Amp turn}}{\text{cm}} = 18{,}750 \text{ oersted}$$

This field, if averaged over the cross-sectional area of the 10 cm bore yields a total flux of:

$$18{,}750 \text{ Oe} \times \frac{\pi (10)^2}{4} = 1520 \text{ kilomaxwell}$$

*Montgomery, D. B., 1969, Solenoid magnet design, Wiley-Interscience, New York.

Thus 9.05 kilowatts per cm is required to equal the flux generated by the permanent magnet.

To cool a 100 cm length of this magnet would require 2.2 liters/sec of water with a 30°C temperature rise, as shown below:

$$9{,}050 \frac{\text{watt}}{\text{cm}} \times \frac{1 \text{ calorie}}{4.18 \text{ watt sec}} \times 100 \text{ cm} \times \frac{1 \text{ deg C} \times 1 \text{ gm}}{1 \text{ calorie}} \times \frac{1 \text{ liter}}{1000 \text{ gm}} \times \frac{1}{30 \text{ deg C}}$$

$$= 7.2 \text{ liters/sec.}$$

In order to equal the 2 ft (60 cm) Alnico V-7 magnet which was assumed, 542 kW should be required, and a flow rate of 4.3 liters/sec of cooling water.

An alternative cooling approach is the boiling of liquid nitrogen. The dissipation of 542 kW would require boiling 0.3 liters/sec of liquid nitrogen.

Another alternative to cooling would be filling the borehole with water and using a snorkel and pump to circulate water in the immediate vicinity of the magnet.

A 542 kW generator would require a 1500 horsepower engine, assuming 50% efficiency.

(3) Superconducting Solenoids. The advantages associated with superconductive solenoids are:

(a) Very high fields of 50 kOe to 150 kOe (but over very small volumes) with no power input required.

(b) There is no necessity to remove massive amounts of heat from the magnet.

(c) Large, bulky power cables are not required.

The disadvantages associated with superconductive solenoid magnets are:

(a) For optimum design, a large dewar is required. A typical configuration would be a 12" dewar surrounding a 3" magnet, with a 1" bore containing a 50 kOe field.

(b) They provide a relatively low flux density when averaged over the cross-sectional area of the entire magnet assembly.

(c) They require careful handling by skilled technicians, and they require a complicated start-up procedure before each use.

(d) They require liquid helium which is cumbersome and expensive to buy and store. Usage estimates range from 1 to 10 liter/hour. The cost is $4.50 per liter.

(e) An expensive development program would be required to get a 5" magnet that would be suitable for downhole operation and a first-cost estimate of magnet price is $20,000 or more.

We have talked to the following manufacturers of superconductive magnets:

Oxford Instruments Incorporated, phone: 301/992-7544, Mr. R. W. Wheatley;

Intermagnetics General Corporation, P. O. Box 566, Guilderland, NY 12084, phone: 518/456-5456, Mr. Garry Morrow;

Advanced Kinetics, 1231 Victoria Street, Costa Mesa, CA 92627, phone: 714/646-7165, Mr. R. W. Waniek;

American Magnetics, Box R, Oak Ridge, TN 37830, phone: 615/482-1056, Mr. K. R. Efferson.

These discussions led to the advantages and disadvantages listed above. In general, it seems that this type of magnet is suited to the generation of strong fields over a relatively small cross-sectional area, as stated in disadvantage number 1 above. When this field is averaged over the diameter of the magnet the dilution of field is obviously great. By using a compromise dewar design, at the expense of increased helium usage, a 2-1/2" bore might be obtained, (Mr. Waniek of Advanced Kinetics), and a flux of the order of 2800 kilomaxwells as shown in figure 5 . The following is a quotation of a letter from Mr. Garry Morrow of Intermagnetics General Corp., Guilderland, N. Y.:

> "As we understand it, your objective is to use a magnet of about 24" winding length to produce the maximum possible flux in a well-casing of 5-1/2" diameter. Allowing for a dewar shell thickness designed to withstand submersion in drilling mud to a maximum depth of 1000 feet, we calculate that it would be feasible to build a magnet generating a flux of 2.8×10^6 Maxwells. The magnet would be designed for persistent current mode operation so that it could be excited at the wellhead and then disconnected from the current source for lowering into the borehole. The magnet dewar would be designed to provide for two hours' operation at steady field between refills of liquid helium."
>
> "We have had some experience with design of cryostats for deep well logging operations. Insulation techniques required for these dewars are rather different from those normally used for cryostats operated above-ground. The operating environment is also characterized by harsh shock and vibration loads not normally encountered by cryogenic superconducting devices."

"Thus, while the magnet winding you require is not particularly difficult, we project a first unit cost somewhat in excess of $30,000. These costs would obviously drop quite dramatically if there were any production potential."

3.2 PRODUCING UNIFORM MAGNETIC FIELDS

3.2.1 With Axial Magnets

In considering how a uniform dc magnetic field might be generated in the rock around a borehole, a magnetic analogy to the well-known guarded resistivity log was hypothesized. For purposes of simplified calculation, it was imagined that isolated magnetic poles (of negligible size) can be used. (While magnetic monopoles have not yet been proven to exist in nature, they can be simulated in practice by using one end of a sufficiently long bar magnet or solenoid.) The resulting field at any point is simply the vector sum of the Coulomb (inverse-square) fields from all the isolated poles assumed, whether magnetic, electric-potential or electric-current fields are considered. For a linear array of poles along the z-axis of cylindrical coordinates (figure 8) there is no tangential (ϕ) component of field, but the z and the r components from all the poles add algebraically. The z and r components of the field gradient are easily formed by differentiation of the field components.

The simplest array to consider would consist only of two shielding poles with no poles between, as shown in figure 8 . The field from two such equal poles of the same sign is shaped approximately as sketched in figure 9 (from Smythe's "Static and Dynamic Electricity," first edition, p. 10). This figure is actually a cross-section through a solid of revolution about the z-axis. We have discovered that this field has the interesting and useful property that it is nearly uniform in strength everywhere within a flattened torus (donut) lying in the center plane of symmetry at a radius $r_o = D/2\sqrt{2}$ from the z-axis, where D is the separation along z of the two equal poles! This is a consequence of the fact that radial spreading-out of the field from the poles is compensated for (within a limited zone) by the crowding-together of the fields from the two poles near the center plane, as seen in figure 9 . It is very convenient that this zone of nearly-uniform field strength is created within the rock at a substantial distance from the borehole (figure 10). The radius of the torus can be varied by changing the pole separation D.

If the rf coils for an EMR system were placed at the origin, it is conceivable that the strongest resonances might arise from this torus-shaped volume of rock. Substantial rf coupling to the torus can be provided by making the length of the rf coil $D/2\sqrt{2}$, parallel to the z-axis. Fortunately, the dc field is near zero in the center zone of the array where the rf coil is located.

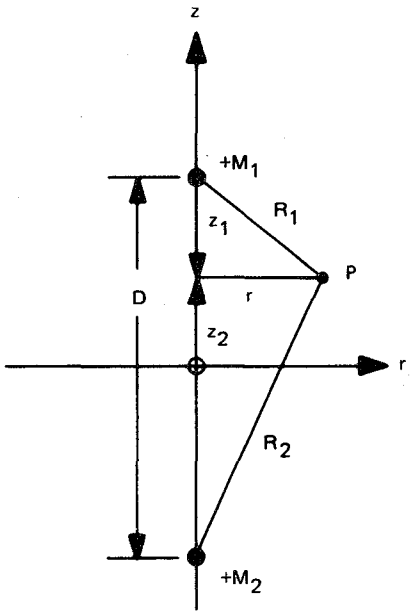

Figure 8. Geometry for two equal charges or poles, M_1 and M_2.

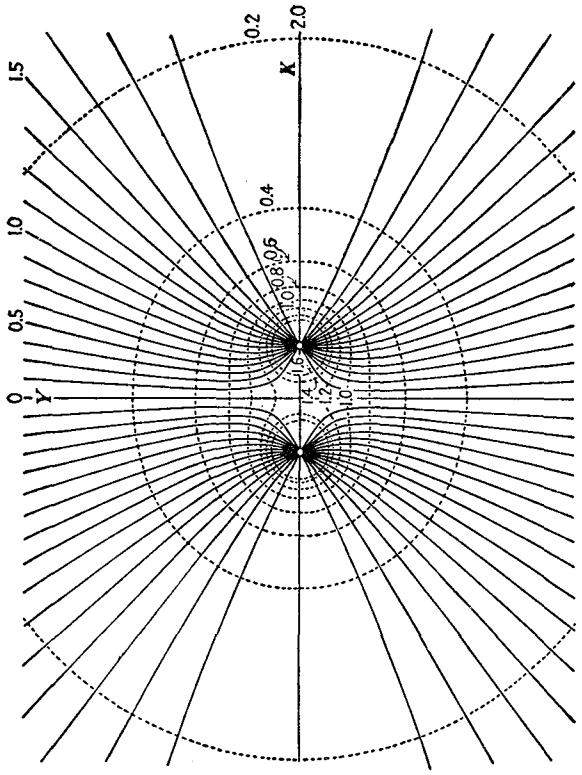

Figure 9. Field about equal charges of the same sign. Lines of force and equipotential lines are shown by solid and dotted lines, respectively.

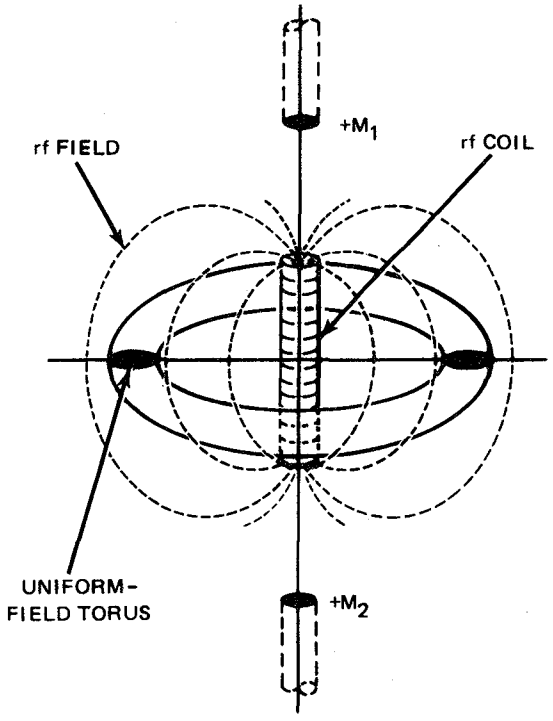

Figure 10. Perspective of proposed configuration.

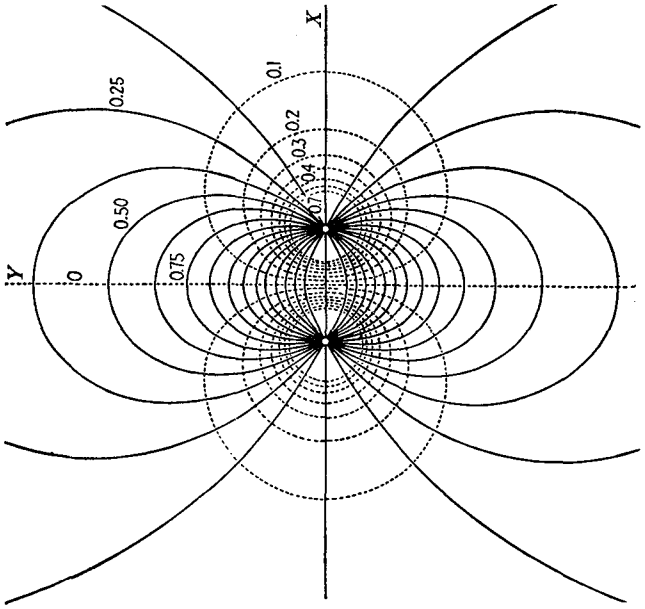

Figure 11. Field about equal charges of opposite sign. Lines of force and equipotential lines are shown by solid and dotted lines, respectively.

The calculations made so far which support some of these surmises are given in the following.

At any point P in the arrangement depicted in figure 8 , the z-component and r-component of the magnetic field from one pole (say M_2) are:

$$ {}_2H_z = \frac{M_2 \cos \theta_2}{4\pi R_2^2} \qquad {}_2H_r = \frac{M_2 \sin \theta_2}{4\pi R_2^2} $$

The total components for both poles are:

$$ H_z = \frac{M}{4\pi} \left\{ \frac{z}{(z^2 + r^2)^{3/2}} - \frac{D-z}{[(D-z)^2 + r^2]^{3/2}} \right\} \qquad (1) $$

$$ H_r = \frac{M}{4\pi} \left\{ \frac{r}{(z^2 + r^2)^{3/2}} + \frac{r}{[(D-z)^2 + r^2]^{3/2}} \right\} \qquad (2) $$

Everywhere on the center mid-plane of the system where z=D/2, ${}_oH_z=0$ and

$$ {}_oH_r = \frac{4 Mr}{\pi (D^2 + 4r^2)^{3/2}} $$

If an array of two poles of opposite sign were employed (figure 11), the field strength components would be given by formulas identical to (1) and (2) except that the signs of the second terms in braces would be interchanged. On the mid-plane the components would be

$$ {}_oH'_z = \frac{2 DM}{\pi (D^2 + 4r^2)^{3/2}} \qquad \text{and} \quad {}_oH'_r = 0 $$

This means that the field strength ${}_oH_r$ for the like-pole case is equal to or greater than that for the unlike-pole case, ${}_oH'_z$, for all radial distances greater than r = D/2. At lesser radii on the center plane, ${}_oH_r/{}_oH'_z = 2\,r/D$. As will be seen, this ratio is $1/\sqrt{2} = 0.707$ at the position of the uniform-field torus, so relatively little field strength is lost by using the like-pole configuration.

Returning to the general expressions (1) and (2) for the like-pole case the four first derivatives are:

$$\frac{\partial H_z}{\partial z} = \frac{M}{4\pi}\left\{\frac{r^2 - 2z^2}{(z^2 + r^2)^{5/2}} + \frac{r^2 - 2(D-z)^2}{[(D-z)^2 + r^2]^{5/2}}\right\} \tag{3}$$

$$\frac{\partial H_r}{\partial z} = \frac{\partial H_z}{\partial r} = \frac{-M}{4\pi}\left\{\frac{3zr}{(z^2 + r^2)^{5/2}} - \frac{3(D-z)\,r}{[(D-z)^2 + r^2]^{5/2}}\right\} \tag{4}$$

$$\frac{\partial H_r}{\partial r} = \frac{M}{4\pi}\left\{\frac{(z^2 - 2r^2)}{(z^2 + r^2)^{5/2}} + \frac{(D-z)^2 - 2r^2}{[(D-z)^2 + r^2]^{5/2}}\right\} \tag{5}$$

In the mid-plane, (4) are zero everywhere and:

$$\frac{\partial H_z}{\partial z} = \frac{8M}{\pi}\left[\frac{(2r^2 - D^2)}{(D^2 + 4r^2)^{5/2}}\right] \tag{6}$$

$$\frac{\partial H_r}{\partial r} = \frac{4M}{\pi}\left[\frac{D^2 - 8r^2}{(D^2 + 4r^2)^{5/2}}\right] \tag{7}$$

These become zero at $r = D/\sqrt{2}$ and $r = D/2\sqrt{2}$, respectively. Since H_z is itself zero, (7) may be the more important in choosing a zone of least magnetic-field gradient. This will be tested. Formula (7) set to zero specifies a circle of radius $r = D/2\sqrt{2}$, lying in the mid-plane of symmetry, coaxial with z. Any small departure from this circle will result in small changes in the magnetic field components ΔH_z and ΔH_r which combine vectorially with the field ${}_oH_r$ on the circle to give the total field change:

$$\Delta H = [(\Delta H_z)^2 + (\Delta H_r + {}_oH_r)^2]^{1/2} - {}_oH_r \tag{8}$$

The two components can be approximated by differentials obtained from (3), (4), and (5) after substitution of $z = D/2$ and $r = D/2\sqrt{2}$:

$$\Delta H_z = \frac{\partial H_z}{\partial z}\,\Delta z + \frac{\partial H_z}{\partial r}\,\Delta r \tag{9}$$

$$\Delta H_r = \frac{H_r}{\partial z}\,\Delta z + \frac{H_r}{\partial r}\,\Delta r \tag{10}$$

Since all the derivatives except (3) are zero on the "a" circle $r = D/2\sqrt{2}$, only the first term of (9) need be used in formula (8) for small z - displacements from that circle. The result after substitutions is:

$$ {}_a(\Delta H)_z \doteq \left\{ \left[\frac{-2M}{\pi D^3} \sqrt{\frac{32}{243}} \Delta z \right]^2 + \left[0 + \frac{4M}{\pi \sqrt{27}\, D^2} \right]^2 \right\}^{1/2} - \frac{4M}{\pi \sqrt{27}\, D^2} $$

Now on the circle "b" obtained by setting expression (6) to zero, the radius is $r = D/\sqrt{2}$ and all the derivatives of (9) and (10) are zero except (5). After the proper substitutions in (10) and (8) we obtain, for a small r - displacement, approximately:

$$ {}_b(\Delta H)_r \doteq \left\{ 0 + \left[\frac{-4M}{\pi \sqrt{27}\, D^3} \Delta r + \frac{4M}{\pi \sqrt{54}\, D^2} \right]^2 \right\}^{1/2} - \frac{4M}{\pi \sqrt{54}\, D^2} $$

In order to compare the two results to find out which circle permits the largest sample volume for a given percentage departure in the field strength, we form the ratios:

$$ \frac{{}_a(\Delta H)_z}{{}_a H_r} = \left\{ \left[\frac{-2\sqrt{2}}{3} \frac{\Delta z}{D} \right]^2 + 1 \right\}^{1/2} - 1, \text{ so } {}_a\left(\frac{\Delta z}{D}\right) \doteq \frac{-3}{\sqrt{2}} \left(\frac{\Delta H}{H}\right) \quad (11) $$

$$ \frac{{}_b(\Delta H)_r}{{}_b H_r} = -\sqrt{2}\left(\Delta r/D\right), \text{ that is, } {}_b\left(\frac{\Delta r}{D}\right) = \frac{-1}{\sqrt{2}} \left(\frac{\Delta H}{H}\right) \quad (12) $$

These are the most restrictive conditions on the dimensions of the sample torus. It can be seen that for circle "a," with $r = D/2\sqrt{2}$, the allowable departure from the circle is three times that for circle "b."

The effects of departures from the two circles in directions at right-angles to those used above are less severe. To evaluate them we may use the (linear) average value of the derivative ${}_a(\partial H_r/\partial r)$ over the interval Δr, and that of ${}_b(\partial H_r/\partial z)$ over the interval Δz, using the corresponding coordinates $r_a = D/2\sqrt{2} \pm \Delta r/2$, $z_a = D/2$ and $r_b = D/\sqrt{2}$, $z_b = D/2 \pm \Delta z/2$ respectively. A number of simplifying approximations can be made where differentials of higher degree occur in polynomial sums. The results, using the appropriate substitutions in (9) and (10), are:

$$\frac{{}_a(\Delta H)_r}{{}_aH_r} \doteq \left\{0 + \left[\pm\frac{16}{3}\left(\frac{\Delta r}{D}\right)^2 + 1\right]^2\right\}^{1/2} - 1 \doteq \frac{16}{3}\left(\frac{\Delta r}{D}\right)^2 \qquad (13)$$

$$\frac{{}_b(\Delta H)_z}{{}_bH_r} \doteq \left\{\left[\frac{2\sqrt{2}}{3}\left(\frac{\Delta z}{D}\right)^2\right]^2 + \left[8\left(\frac{\Delta z}{D}\right)^2 + 1\right]^2\right\}^{1/2} - 1 \doteq 8\left(\frac{\Delta z}{D}\right)^2 \qquad (14)$$

Expressions (13) and (14) have been expanded and simplified using the binomial theorem. They may now be tabulated together with (11) and (12) for a range of assumed permissible values for the variation in field strength (in terms of a ratio $\Delta H/H_r$):

$\Delta H/H_r$:	10^{-2}	10^{-4}	10^{-6}	
(11) :	2.1×10^{-2}	2.1×10^{-4}	2.1×10^{-6}	$r_a = D/2\sqrt{2}$
(12) :	0.71×10^{-2}	0.71×10^{-4}	0.71×10^{-6}	
(13) :	0.43×10^{-1}	0.43×10^{-2}	0.43×10^{-3}	
(14) :	0.35×10^{-1}	0.35×10^{-2}	0.35×10^{-3}	$r_b = D/\sqrt{2}$

The numbers in rows (11) and (13) give one-half the approximate cross-sectional dimensions of the useful sample volume for ring "a". Rows (12) and (14) give half the cross-sectional dimensions for ring "b". Although ring "b" would have twice the perimeter of ring "a", its volume is only 55% that of "a", and it is located in a field H_r that is only 70% as strong. Clearly, the flattened torus of radius $r = D/2\sqrt{2}$ is a better place to have the rock sample.

It remains to compare the field uniformity and strength available in this torus using a like-pole array with those obtained with an unlike-pole array as in figure 11. In this figure, the most uniform field is again in the center plane $z = D/2$, especially in the borehole at $r = 0$. This is undesirable. In the rock outside the hole within this plane, $H_r = 0$ and ${}_oH_z = \dfrac{2MD}{\pi\,(D^2+4r^2)^{3/2}}$, which is

equal to ${}_oH_r$ for the like-pole case at r = D/2; on the "a" ring where r = $D/2\sqrt{2}$, the field strength for unlike poles in $\sqrt{2}$ times stronger than that for like poles. On the "b" ring where r = $D/\sqrt{2}$, the field strength for unlike poles is $\sqrt{2}$ times weaker than that for like poles. It appears that the two arrays are reasonably equivalent in field strength within the rock.

The four field derivatives for the unlike-pole case are identical to expressions (3), (4) and (5) except that the center signs within the curly braces are all reversed. In and near the mid-plane, the expressions equivalent to (3) and (5) are essentially zero and only expressions equivalent to (4) need be evaluated. On the center plane these become:

$$\frac{\partial H_r}{\partial_z} = \frac{\partial H_z}{\partial_r} = \frac{-24\ M\ Dr}{\pi\ (D^2+4r^2)^{5/2}} \qquad (15)$$

These derivatives are zero only on the axis where r = 0. At rings "a" and "b", they compare with the largest derivatives (6) and (7) for the like-poles case as shown by the ratios tabulated below:

	Ring a	Ring b
radius r :	$D/2\sqrt{2}$	$D/\sqrt{2}$
ratio: $\frac{(15)}{(6)}$	$\sqrt{2}$	∞
ratio: $\frac{(15)}{(7)}$	∞	$\sqrt{2}$

Hence it can be seen that the uniformity of the magnetic field is substantially worse in both directions for the unlike-pole case, at these radii within the rock on the mid-plane. At lesser, arbitrary radii which might be chosen just outside the borehole, the comparison is as follows:

radius r	D/5	D/10	D/20	D/50	D/100
ratio: $\frac{(15)}{(6)}$	0.65	0.31	0.15	0.060	0.030
ratio: $\frac{(15)}{(7)}$	1.76	0.65	0.31	0.12	0.060

This means that the field near the borehole would generally be more uniform with the unlike-pole array, as well as much stronger.

The field strength on the axis and the mid-plane with the unlike-pole array is given by ${}_oH_z = M/\pi D^2$, while that at circle "a" with the like-pole array is given by ${}_aH_r = 4M/3\sqrt{3}\,\pi D^2$, and the former is 1.3 times as strong. This does not clearly favor one array or the other. The choice must probably be made on the basis of the desired probing depth (out from the borehole), expected interference from borehole fluid, and usable sample volume in the two cases.

Examples of the field strength attainable can readily be calculated, assuming various pole spacings D and pole strengths M, say for the like-pole array at ring "a". Magnets are always specified in terms of the maximum field generated, H_m. The highest steady values of H_m attained are of the order of 500,000 oersteds for cryomagnetic solenoids. A value of 100,000 oersteds might be practical to assume as the average field emerging from one end of a long solenoid. The pole strength $M \approx H_m$ x area. Area can be taken to be about half the cross-section of the borehole, assumed to be either 5-inch or 2-inch. Some numbers resulting from these assumptions are listed below:

Values of ${}_aH_r$, oersteds

Hole dia., M (Oë in.^{2})	D = 5 in.	D = 10 in.	D = 20 in.	D = 40 in.	D = 80 in.
5 in. 10^6	9,800	2,450	612	153	38
2 in. 1.5 x 10^5	1,472	367	92	23	5.7

Such values should greatly help in increasing the strength and reducing the ratio: (line width/line frequency) for an EMR signal, since they are all orders of magnitude stronger than the earth's magnetic field of about 0.5 gauss.

3.2.2 With Transverse Magnets

In the above, the generation of quasi-uniform magnetic fields in the rock around a borehole by means of in-line arrays of magnetic poles was treated analytically. Unfortunately, the volume of the constant-field toroid was found to be rather small, for selected maximum values of the magnetic gradients. One cause is the rapid spreading of monopole fields in three dimensions. If one were to consider the field outside the center part of a bar magnet (near the mid-plane between two unlike poles), it can be seen that greater uniformity (a lower gradient) in a direction parallel to the bar axis could be achieved by lengthening the bar. There might be some hope also of reducing the radial gradient over a limited volume by canceling part of the close-in, stronger field with a short, coaxial magnetized sleeve of opposite polarity placed around the center of the bar, since such a sleeve could be adjusted in three respects: its length, diameter and strength.

Such an in-line magnet system has not yet been studied quantitatively. Instead, it appears likely that we need to use crossed, transverse borehole coils for Béné's NMR methods*. The more uniform the field which can be produced in the sample region, the longer the signal bursts (figure 3) can be made to last and the easier they will be to see. Hence, we undertook to study how the field of a transverse coil might be made more uniform by means of bucking coils in a manner similar to that postulated above for in-line arrays.

For a transverse coil many times longer than its "diameter", the field fringing at the ends can be ignored and the problem for the central portion of the coil is reduced to a two-dimensional one.

Assume the cross-section shown in figure 12. The main coil generates the field shown by the arrows. The most uniform part of this field is that near the plane z = 0. This portion of the sample can be selected for assaying by placing the secondary coils as shown (in practice, these too would be elongated in the x-direction, at right angles to the page). Hence, only the magnetic gradients in this region need be considered.

Because of symmetry, there is no y-component of the field at the z = 0 plane. The main coil is equivalent to two current sheets of width B, separation A, and current density I per unit width. The total field at the z = 0 plane can be found by integrating the expression for a bililar circuit (from W. R. Smythe's Static and Dynamic Electricity, McGraw-Hill, 1939, p. 266), as follows:

$$(B_z)_s = 2\mu I \int_{-B/2}^{+B/2} \left[\frac{y + A/2}{(y + A/2)^2+z^2} - \frac{y - A/2}{(y - A/2)^2+z^2} \right] dz \qquad (1)$$

$$= 4\mu I \left[\tan^{-1}\left(\frac{B}{y + A/2}\right) - \tan^{-1}\left(\frac{B}{y - A/2}\right) \right] \qquad (2)$$

The field from the compensating current-sheet coil, which may have different values of A, B, and I, is given by a similar expression. If formula (2) is plotted vs the radial position y, a curve asymptotic to $(B_z)_s = 0$ will result. The curve representing the opposite field of the compensating coil can presumably be adjusted to intersect that of the main coil at two or more points (if inverted in sign) as shown in figure 13, hence, to cancel out most of the gradient in a limited region, without canceling all of the field. This would result in a nearly-uniform field over this region.

*Another reason for using such coils will be seen in part 3.4; for the same size and power, the transverse coils generate a much stronger external magnetic field H_o at a distance of one diameter out from the center.

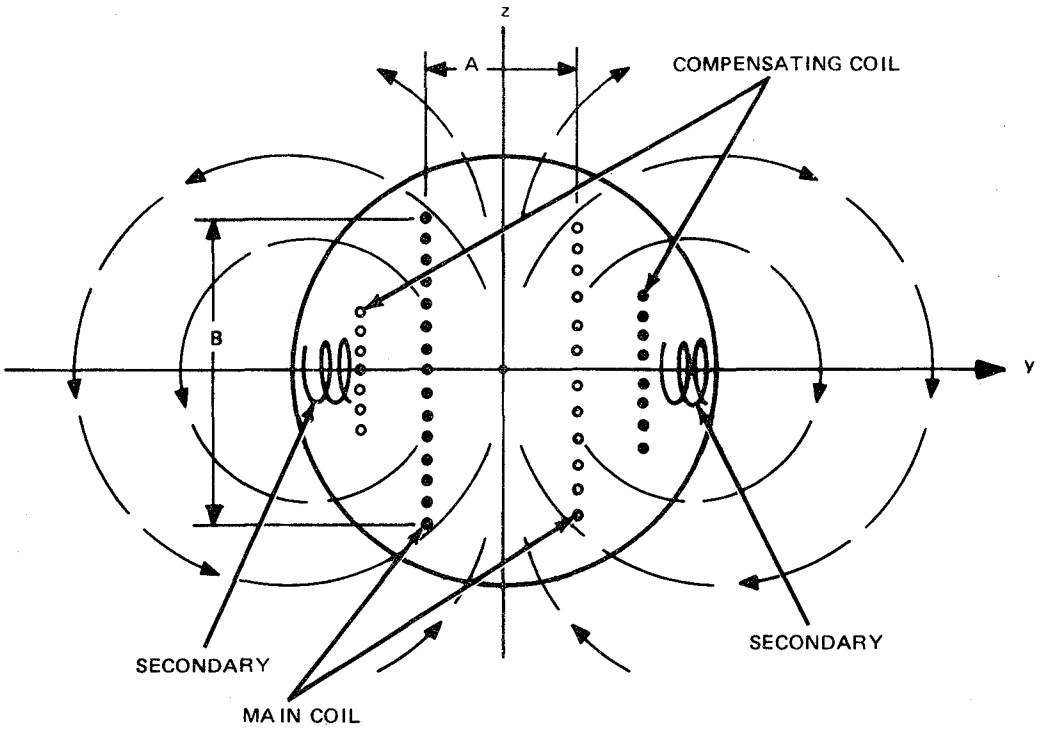

Figure 12. Cross-section of transverse coil system with gradient compensation at y-axis

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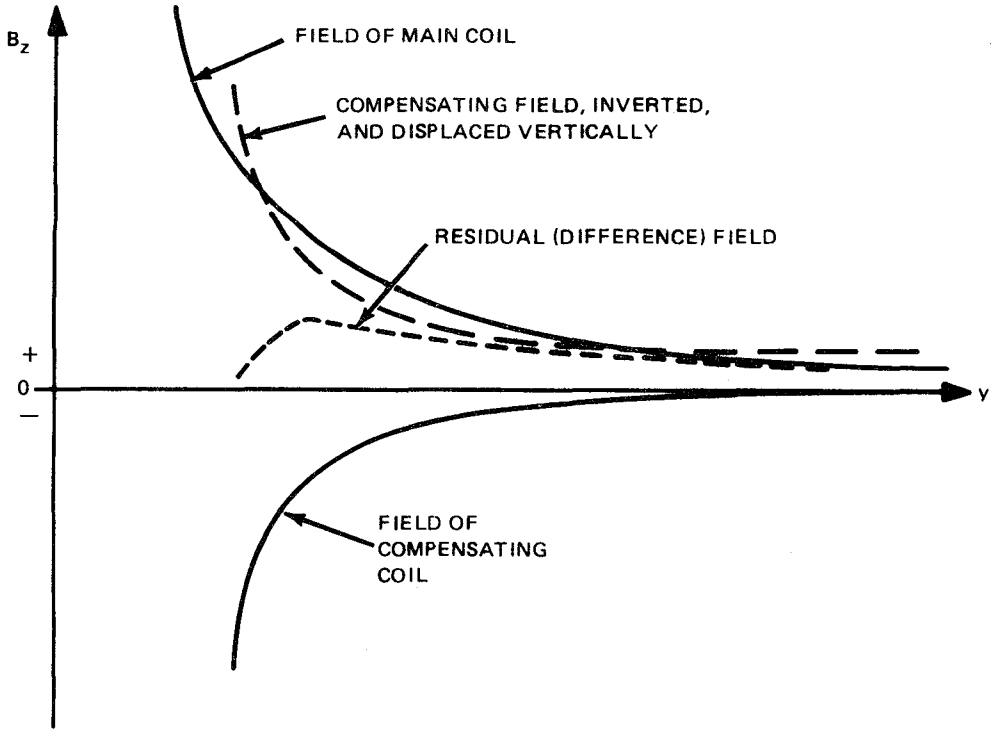

Figure 13. Strength of z-fields vs position along y-axis, illustrating graphical method of selecting compensation parameters

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Efforts to find analytical solutions specifying the necessary relationships between the two values of current, spacing and width have been unsuccessful because of the transcendental form of formula (2). Even attempts to do this for simple pairs of current filaments [using only the integrand of formula (1) to give the field] failed because a continuum of solutions was found without sufficient criteria for choice. An assumption that the curves could be made to intersect at three points resulted in a quartic equation, for which no general method of solution is at hand. However, it can be said from the theory of equations that one pair and perhaps both pairs of the four solutions are probably complex or imaginary.

Lacking analytical solutions, we had formula (2) plotted for several discrete values of I, A, and B using the Teledyne Geotech scientific computer. Two sets of these plots are shown in figure 14. The abscissae represent values of y/A where B is whatever fraction of A is shown on the caption. The (negative) ordinate is the function in the brackets of formula (2). This times the value of I (which increments by unity for successive curves) gives 1/4 the field strength in gauss where I is in emu (1/10 of its value in amperes).

Pairs of these curves can be superimposed on a light table and shifted vertically to find a good fit (this sometimes requires interpolations). There are generally two intersection points. The vertical separation of the x-axes then gives the residual field in the zone of good cancellation. Table 1 lists several good fits obtained in this way which provide "recipes" for construction of a uniform-field transverse magnet system.

Table 1. Some compensated transverse magnet designs

	Main coil			Compensation			Cancellation	Max. misfit,	Resid. field,
Solution	A	B/A	I	A	B/A	I	zone y/A	gauss/4I	gauss/4I
1	1	0.8	2	1	0.2	5.7	1.7 to 2.7	0.006	0.12
2	1	0.8	1	1.5	0.13	1.0	1.2 to 1.8	0.010	0.22
3	1	0.4	3	2	0.1	1.3	1.5 to 1.8	0.005	0.31
4	1	3.2	3	1	0.8	5.0	3.5 to 5.2	0.010	0.25
5	1	3.2	3	1	1.6	2.3	2.2 to 3.4	0.015	0.38
6	1	3.2	1	2	0.1	5.0	5.8 to 10	0.003	0.03

As table 1 shows, the use of a compensating coil of different geometry from the main coil can indeed produce an external field that is nearly uniform, within a few percent, over a zone comparable in thickness to the coil "diameter", which begins about one coil-diameter away from the near edge of the coil. This is very hopeful. The chief drawback is that half or more of the field strength must be canceled to achieve this uniformity. However, the plots provide an almost infinite number of design choices, the best of which can be selected when the most important constraints have been determined.

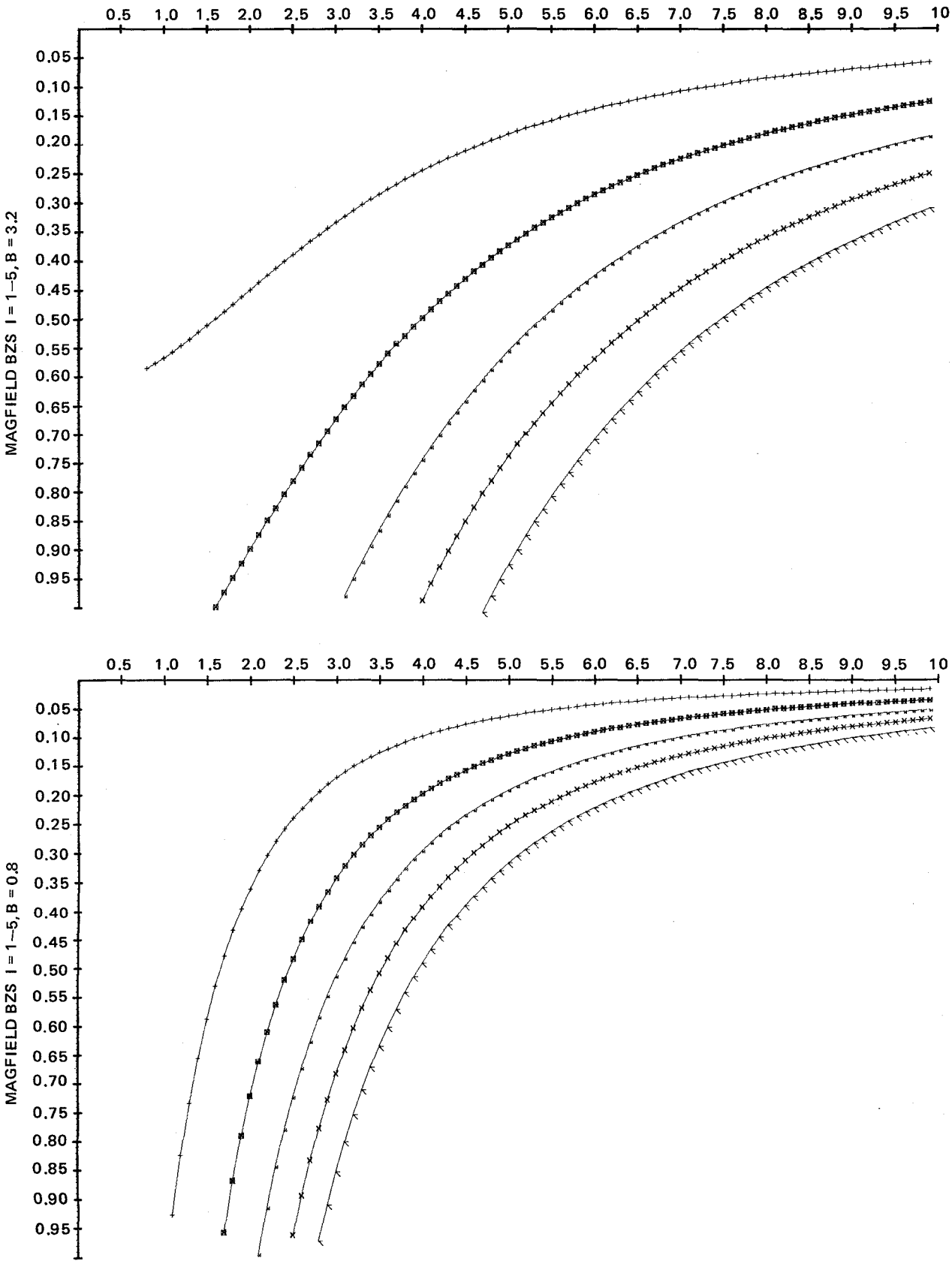

Figure 14. Plots of magnetic field strength (B_z)s vs radial distance from axis of a transverse coil, for two coil widths B, equal "diameters" A, five values of current I

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It should be remembered that this analysis has been concerned only with the radial uniformity of the field. Azimuthal (vs. y) uniformity can probably also be achieved by varying the value of I over the width of the coil and by curling the current sheets. However, this introduces additional variables. A workable design can probably best be found by direct analog model tests guided by intuition. If better accuracy is ever needed, a multi-dimensional model test could readily be performed by computer. The considerable programming expense is not yet justified, since we are still making order-of-magnitude choices in other phases of the overall problem.

3.3 THE RAPID-SWITCHING PROBLEM

The NMR techniques of Béné's group in Switzerland, and many of those disclosed in the well logging patents, require rapid quenching of strong magnetic fields. This is not easy to do. We have therefore studied the governing physical principles, at least for transverse loops.

For a loop of N turns and radius r centimeters carrying a current of i abamperes, the field strength H near the center is:

$$H = 2\pi Ni/r \quad \text{(oersteds) or emu} \tag{1}$$

The total energy W stored in the whole magnetic field is given in standard texts by:

$$W = (\mu/8\pi) \int_V H^2 dv \text{ (ergs)}. \tag{2}$$

The integration should be performed over all of space. This would be difficult because the general formula for H from a loop at any point in space is very complicated and contains elliptic integrals. It is sufficient for our purpose to obtain an order-of-magnitude result by physical intuition: the field H can be considered constant and confined to the volume of a sphere fitting within the loop. Combining (1) and (2) then gives:

$$W \approx (\mu/8\pi)\ (4\pi^2\ N^2 i^2/r^2)\quad (4\pi r^3/3) \tag{3}$$

$$= (\mu r N^2 i^2/0.15)\text{ergs} = (\mu r N^2 I^2/15 \times 10^7)\text{ joules.}$$

where I (amperes) = 10 i (abamperes)

If the current I is interrupted and the energy W is dissipated in an avalanche diode of voltage threshold E volts, we know from observation that the current decreases linearly with time to zero from its initial value I_o. The average rate of energy dissipation is therefore $EI_o/2$ joules/second. The turn-off or switching time is simply:

$$t = W/(EI/2) \approx \mu r N^2 I/8Ex10^7 \text{ seconds.} \tag{4}$$

Usually, $\mu=1$. We are also faced with the requirement to make H> 100 oersteds. Substituting from formula (1),

$$t \approx Nr^2/5Ex10^4 \text{ seconds.} \qquad (5)$$

It can be seen from formula (5) that, for a prescribed field strength, the effective radius r of the loop is the parameter with the greatest influence on the turn-off time. For a rectangular, "transverse" loop coil, r is some function of both the width and length. The width must always be made as great as possible for the available borehole diameter. The length should be several times the width to get the best field shaping within the rock. Hence, r is essentially not very adjustable. The remaining parameters N and E can be adjusted within certain practical limits. Table 2 lists several combinations of possible practical interest, together with the current I necessary to obtain H=100 oersteds, obtained from formulas (5) and (2).

Table 2. Some approximate loop designs

Effective loop radius r	Time t, micro sec.	Loop turns N	Transient voltage E	Required current I
10 cm (5-inch hole)	1	1	2000 v.	1600 a.
	1	3	6000 v.	533 a.
	10	1	200 v.	1600 a.
	10	10	2000 v.	160 a.
4 cm (2-inch hole)	1	1	320 v.	640 a.
	1	10	3200 v.	64 a.
	10	4	128 v.	160 a.
	10	40	1280 v.	16 a.

It must be borne in mind that the calculated values of E and I listed in table 2 are possibly in error by a factor of 2 or 3 either way, because of the simplifying assumptions made regarding the field geometry. Nevertheless, they provide some guidance in showing that fairly large currents and voltages must be dealt with to achieve a sufficiently short switching time for solid samples, with adequate field strength. This governs the choice of power supplies, switching devices, and loop conductor sizes. We can also see that a loop with only one or a few turns is required, as might have been surmised from formula (4), wherein N is the most important parameter affecting the turn-off time t. This departs considerably from conventional magnetometer practice and from the techniques employed by the Swiss for liquid samples, wherein coils of over 1000 turns are used.

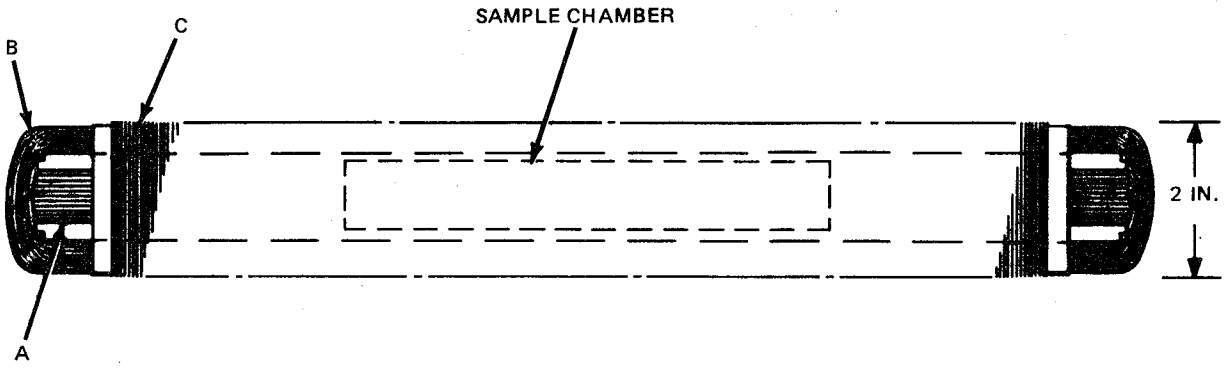
3.4 SOME FIELD-GENERATION EXPERIMENTS

It happened that we had already built a coil (A of figure 15) and a switching circuit (the left-hand half of figure 16) which are able to handle currents and voltages approaching those shown in the last line of table 2, with an appropriate loop diameter and number of turns. (With this combination, we could test the prediction of table 2 regarding shut-off time.) In the process of developing this circuit with the coil current (hence field) monitored on an oscilloscope connected across a 0.1 ohm series resistor, it had been learned that 5 amperes flowing in coil "A" could not be turned off in less than 1 millisecond by any type of switch with any combination of switch capacitors, parallel damping resistors, and diodes. A series resistance of 8 ohms shortened the switching time to 80 microseconds. In the magnetometer literature (section 2.5.2) we had encountered the circuits in figure 17(b) and (c). From our own studies (section 3.3 above) we deduced the circuit of figure 17(d). All of these were tested. It was found that the shortest current-fall times were achieved with the circuits of figures 17(c) and (d). Since the avalanche-diode circuit (figure 17d) is the simplest and most convenient (using Varo 550 volt avalanche diodes to protect the solid-state switches from accidental avalanching), it was used in the breadboard of figure 16.

Tests of the field strength generated by the three coils of figure 15 were made, using a gaussmeter with a 1/16 x 1/4 x 2 inch Hall-effect probe. The right-hand columns of the table in figure 15 show the results, normalized to 1 ampere of coil current. H_i was measured inside the coils and H_o outside, 1 inch from the coil surface near the center. The probe was always oriented for the maximum reading. Figure 15 shows a striking contrast between the outside field H_o produced by the long solenoid C and the two long, rectangular, transverse coils A and B, for similar values of current and internal field H_i; the latter are about ten times as effective. However, none of these coils would be capable of producing the required prepolarizing field of 100 gauss or more in an external sample (the rock around a borehole). That would require a current of 60 amperes for several seconds, which would dissipate 1800 watts, in even coil A, and could quickly melt it.

To investigate the possibility of producing larger external magnetic fields by using permeable cores, experiments were run with various available samples of ferrite and powdered iron. These materials were chosen to retain the capability for rapid field quenching. By testing them as the cores of a 5-turn coil connected to an rf impedance meter, all these materials were found to be capable of operating up to at least 10 MHz without excessive loss (the power factor remained below 10%). By inserting the gaussmeter probe into a narrow transverse slit in a long cylindrical core of each material wound with a large coil, the induction B could be measured; it was found that magnetic saturation occurred at 3000 to 4000 gauss in the ferrites and about 13,000 gauss in the powdered iron.

Because of the findings of figure 15, effort was concentrated on transverse coils. Because of patent coverage of elongated coils such as (A) of figure 15 (see section 2.5.3), a coil array was built, as shown in figure 18. The spherical windings would use up all the available space in a borehole tool about 6 inches in diameter. They could provide 7500 ampere-turns of magnetomotive force (MMF) for a short time, but were used for extended periods



COIL	TURNS	WIRE	OHMS	mH	f_o, kHz	Q 1 kHz	(1 AMP) H_i	(1 AMP) H_o
A	50	#16	0.55	0.63	425	7.5	12 G	1.6 G
B	150	#23	4.7	2.5	280	3.3	18 G	1.6 G
C	400	#23	4.6	1.5	462	2.0	18 G	0.16 G

Figure 15. Three-axis NMR test coil

G 9473

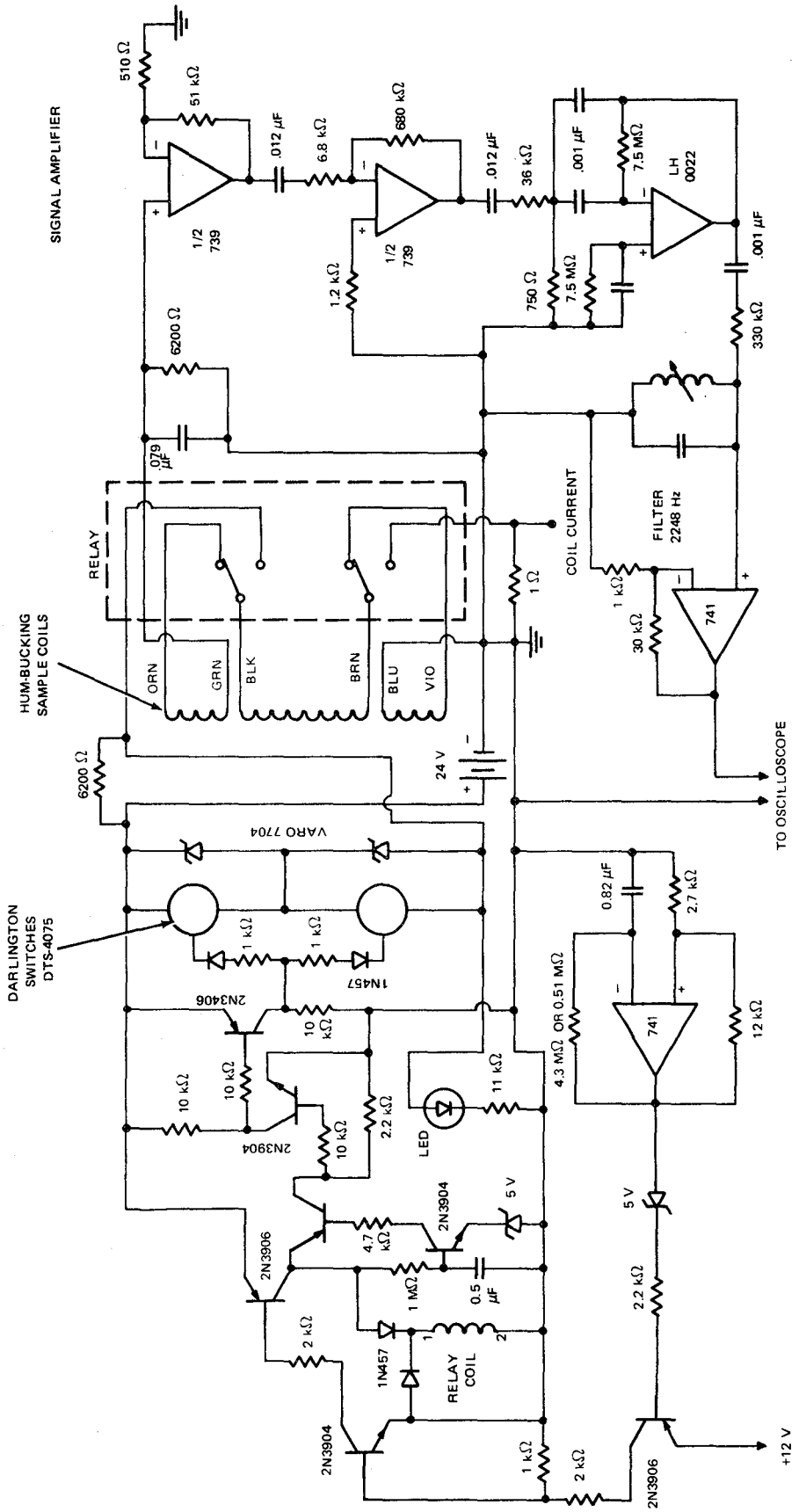
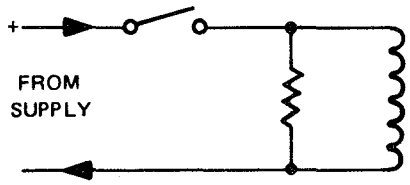
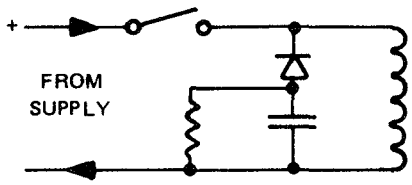


Figure 16. Schematic of NMR breadboard

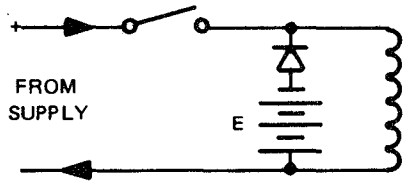
G 9761



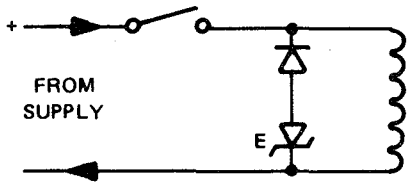
(a) Damping resistor



(b) Diode and capacitor



(c) Diode and battery



(d) Diode and Zener

Figure 17. Various arrangements for quenching the current in a coil

G 9762A

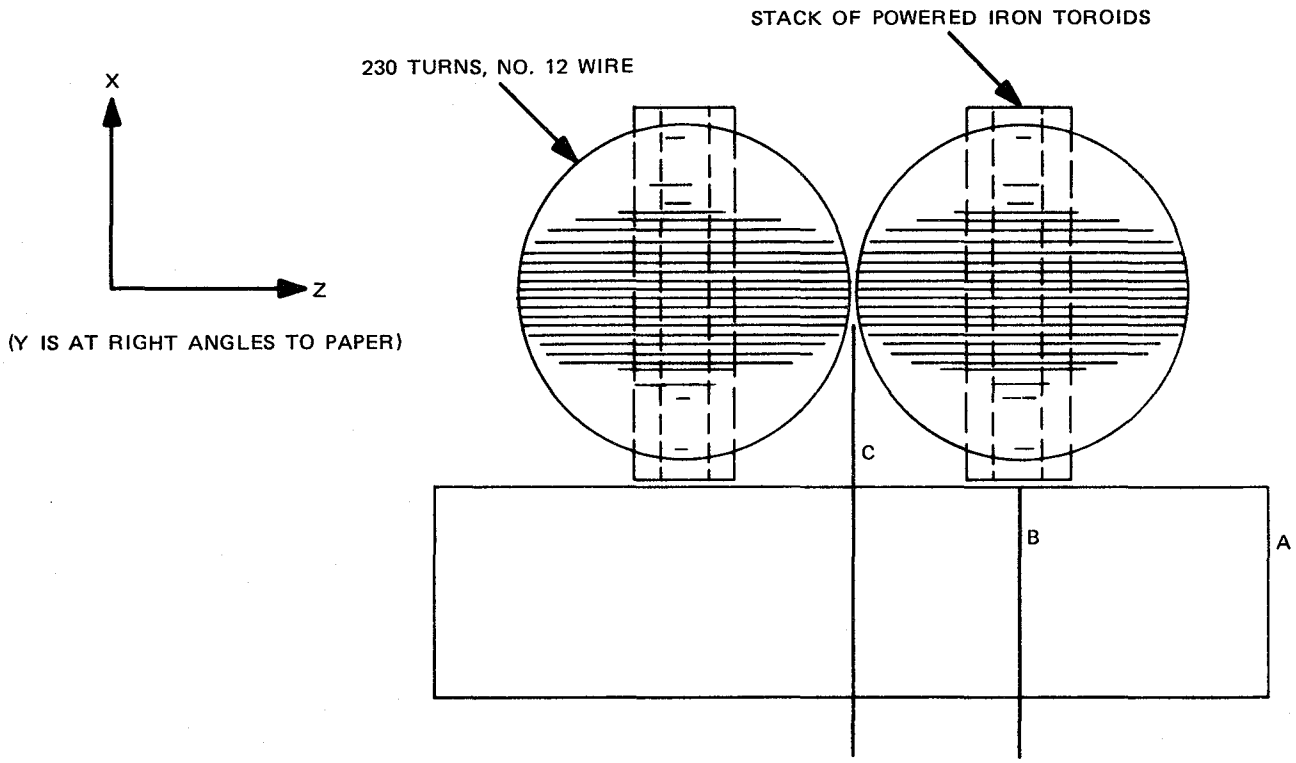


Figure 18. Spherical, cored coil array

at 10 amperes (2300 ampere-turns). Fewer turns of larger wire, with more current, could be used for faster quenching.

The cores were made of 5-1/2 inch long stacks of 1-1/2 inch O.D. powdered-iron toroids of square cross-section. The core shape was a compromise between high effective permeability (which depends mostly upon the ratio: length/diameter--see figure 7) and large cross-section; it is not necessarily the optimum. They were operated well below saturation.

The external field generated by this array was plotted in three planes (A, B and C of figure 18) by means of the gaussmeter probe. Its optimum orientation gave the direction of the field and its total value at each location. The results are shown in figures 19, 20 and 21 for the 10-ampere coil current. The broken curves are equipotentials (contours of constant total field strength). The field directions are indicated by thin, solid curves.

Figure 19 is a cross-section of the external field produced when the two coils are connected with opposite polarities. It partly simulates the field to be expected from "magnetic poles of opposite sign" produced by two long, separated magnets (figure 11). For these particular magnets, field strengths up to 200 gauss are seen to occur in the external sample volume. However, the gradients are strong throughout. The pattern in the x-y plane "B" is similar to half that of figure 19.

Figure 20 is a cross-section of the external field from a transverse array with like-polarity magnets. Essentially the same pattern would be repeated (except for the end sections) in a longer array of several magnets, simulating the field of an elongated transverse coil. This field partly simulates that from two long axial magnets with like poles together (figure 9).

The outer contours, for field strengths of 50 gauss or less, approach cylinders in the central region of the array. This means spreading in only two dimensions, and smaller gradients. Closer spacing between successive magnets would improve this effect. However, with the present spacing, there is a region of almost constant field around the mid-plane of the array, with a field maximum of 53 gauss. Figure 21 displays this interesting region in the transverse, x-y plane "C". The two figures together indicate that there is a region of about 2 $in.^3$ (shaded) in which the magnetic field strength is constant to within ±3%, centered one inch outside of the wall of the "logging tool." The field strength is about 50 gauss. This would be the most favorable region for an NMR sample. Fortunately, there is room near it, in the mid-plane "C" for transverse solenoids or cored coils to couple an orthogonal field to this sample volume. In any future work, this coil arrangement should probably be exploited.

It should be re-emphasized that rapid quenching of strong magnetic fields is necessary, for the Swiss (Béné) NMR techniques or for most patented NMR logging techniques. These techniques, in turn, are probably necessary for the testing of appreciable sample volumes outside of a well bore (hence, good signal strength), where magnetic fields are relatively non-uniform. Steady fields, as from a bar magnet, are not expected to be very effective because of the small sample volume; see section 3.2.1 for estimates.

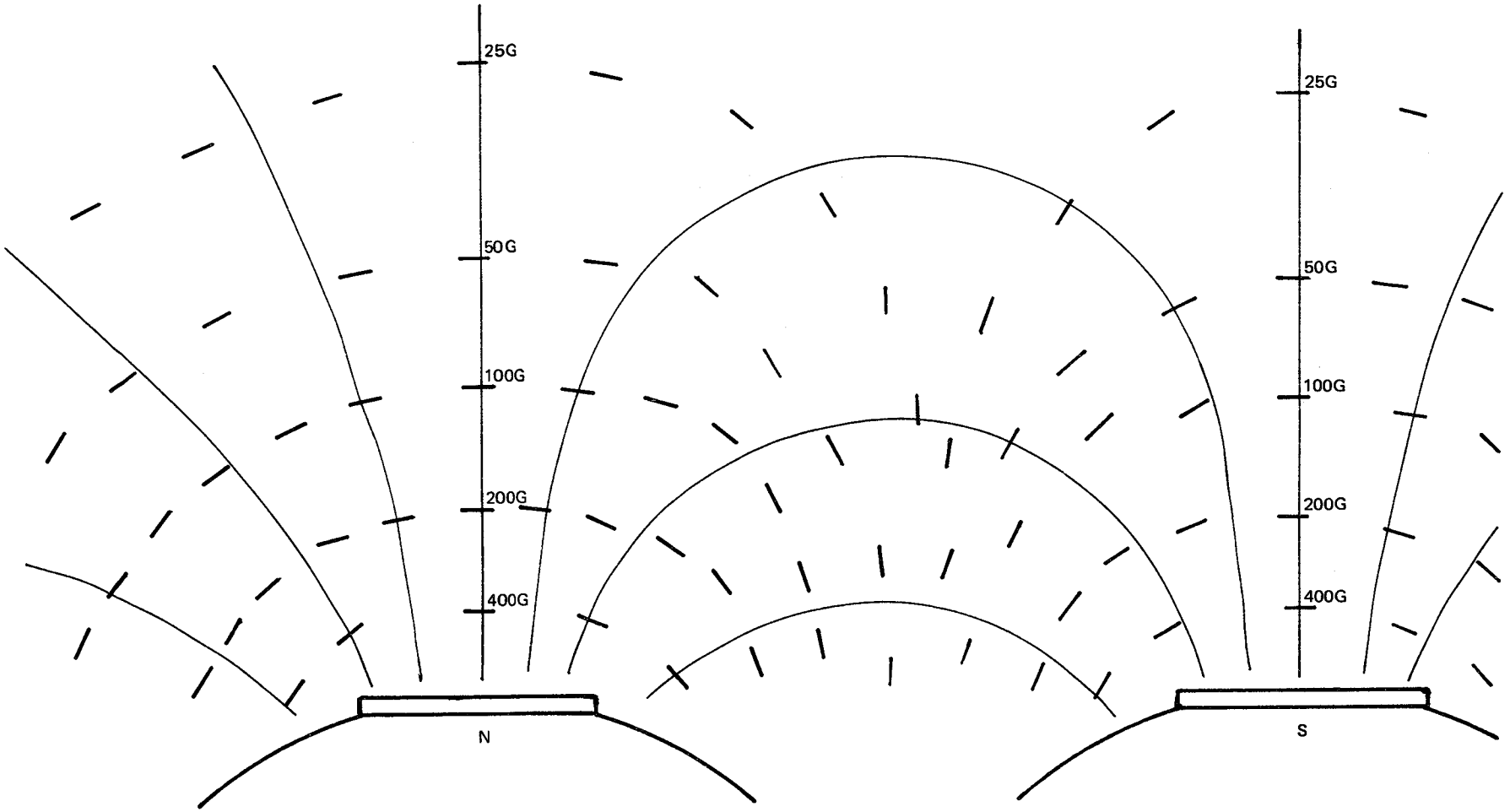


Figure 19. Field pattern in the x-z plane "A" for opposite-polarity magnets

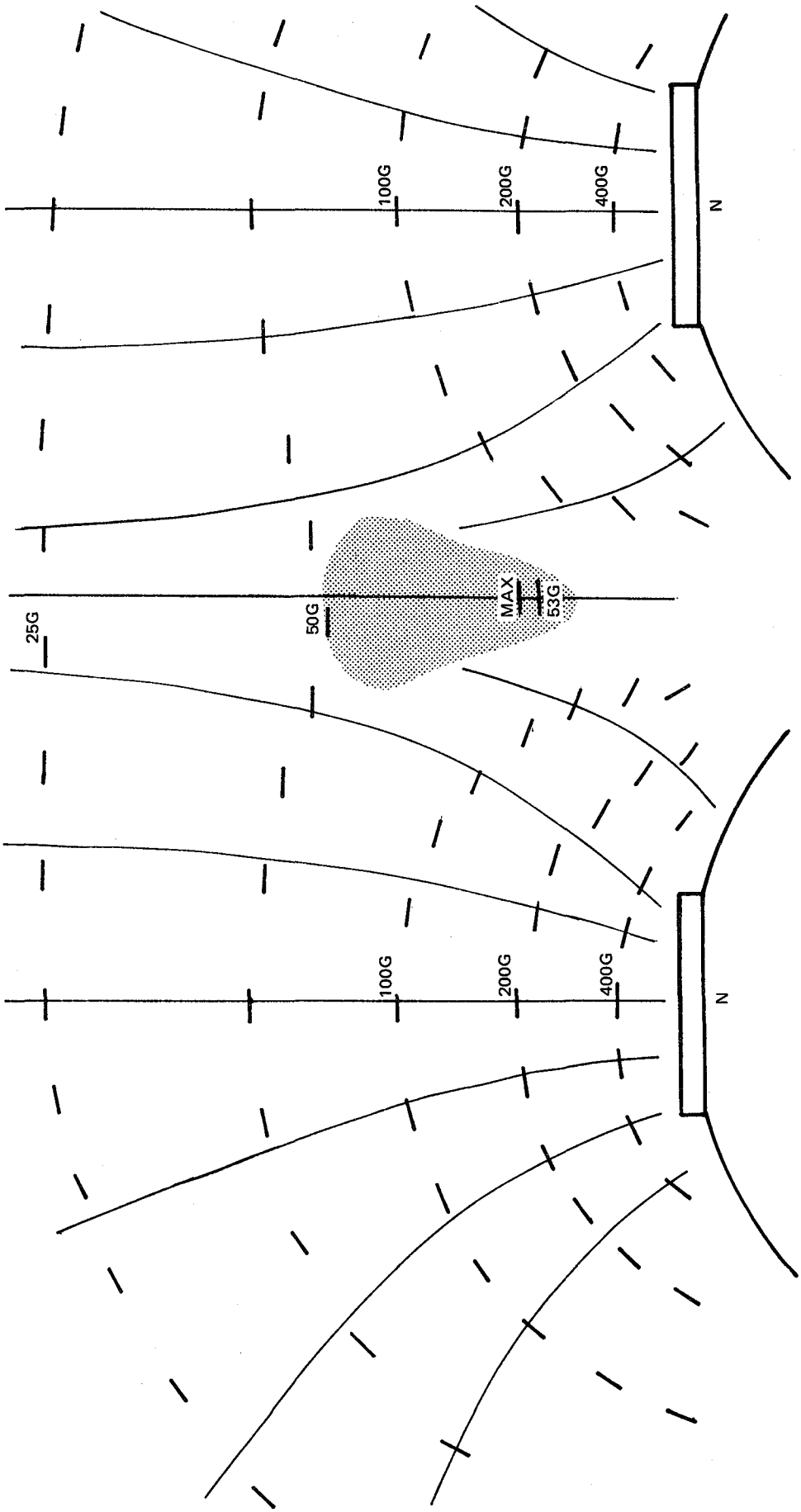


Figure 20. Field pattern in the x-z plane "A" for like-polarity magnets

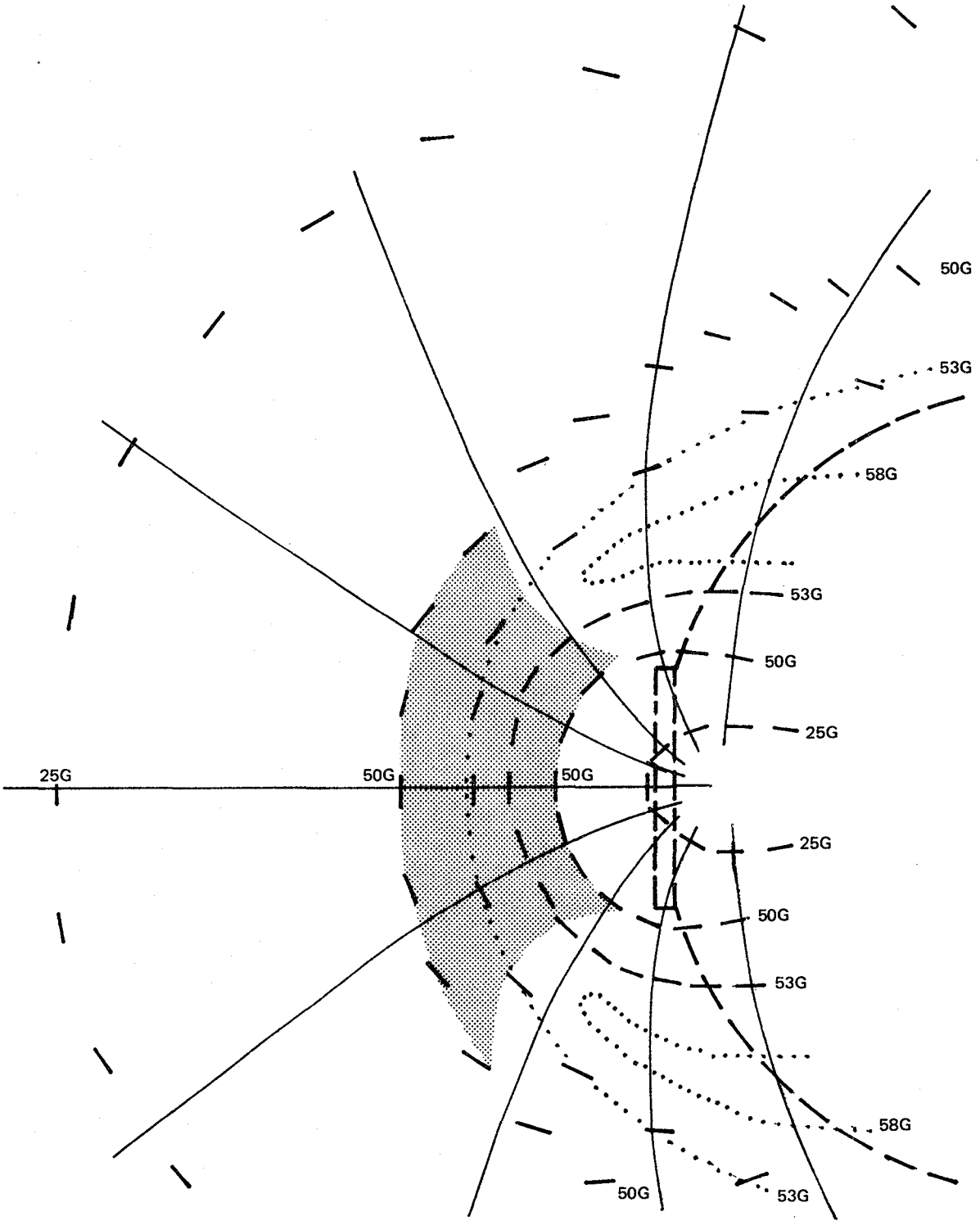


Figure 21. Field pattern in the x-y mid-plane "C" for like-polarity magnets

4. SELECTION OF INDICATOR SUBSTANCES

From our previous work under an ARPA/Bu Mines contract on the NQR (nuclear quadrupole resonance) effect in minerals, we knew that useful EMR responses can be expected from only certain elements in certain substances. For assaying, we considered it essential to obtain a diagnostic indication directly from the substance of economic interest---not its water of hydration, its impurities, nor its crystal form. Consequently, the decision was made early in the program to aim at using the NMR (nuclear magnetic resonance) variety of EMR. NMR can identify many economic minerals by the uniqueness of the Larmor frequencies of the major element of interest. This is true of many metallic ores, for example. Hydrogen gives the strongest NMR signal of any element, but is not a useful indicator of any mineral except oil or "oil shale", because water is widespread in the earth. Since the identification of petroleum by NMR logging has received much attention from the oil industry, and there is not yet a viable oil shale industry, we decided to concentrate on other important but neglected minerals. Those applications should be pursued first which promise the greatest early practical benefit.

The selection process included study of the NMR and economic-geology literature, a large number of telephone calls to mining people all over the U. S., sample-collecting visits to a number of mines, and NMR tests of actual U. S. mineral samples at nearby laboratories.

4.1 NMR-RESPONSIVE ELEMENTS OF ECONOMIC INTEREST

The initial choice of indicator substances appeared to be subject to the following definite constraints:

(1) The substances chosen should be elements of high intrinsic commercial value;

(2) The most abundant isotopes of such elements should give a strong NMR signal. This means: (a) a large gyromagnetic ratio, and (b) a small or zero quadrupole line-splitting effect;

(3) These elements should currently be the main products of large U. S. mining activities;

(4) Mining exploration for these elements should be able to benefit from borehole assays.

We tried to evaluate all these factors with respect to all the elements in the periodic table. Most very heavy elements can immediately be eliminated because they have no long-lived (hence naturally-occurring) isotopes. All the noble gases, except perhaps helium, plus bromine and iodine, can be omitted because they are not known to occur in underground concentrations. A large number of other elements can be eliminated because their NMR - active isotopes, if any, comprise only a minuscule proportion of the total of that element; this is the case with oxygen, uranium, sulfur, and calcium, unfortunately. A few important elements, particularly iron, nickel, thorium and

cerium, have no stable isotopes with a nuclear magnetic moment, hence do not exhibit NMR. Of the 86 elements remaining, a large number can be ignored because they are not yet of any known commercial importance, or are mined only as minor by-products of mining for other associated elements. This is the case with the platinum and palladium families of metals, with most of the rare earths, and in most cases with gold, silver, and several minor metals. With gold, silver, and many other truly rare elements, concentration in the ore is generally less than 1%, which would make detection by NMR difficult. In addition, gold and silver, among others, provide only a weak, low-frequency NMR effect.

What remains? Table 3 is an attempt to list the commercially important elements in the order of their amenability to measurement by NMR. The criterion was: (Larmor frequency at 10 kG) x (isotopic abundance). The electric quadrupole moment Q is also listed where available (in E. R. Andrew's Nuclear Magnetic Resonance, Cambridge U. Press, 1969, p. 224). Table 4 lists the remaining elements for which NMR logging might become useful under the right circumstances. These are listed in order of atomic number.

Hydrogen is included in table 3 because of its possible value in assaying petroleum, oil shale, waters of hydration, and free moisture content in some minerals and rocks. In table 4, several elements of great commercial importance in the United States are to be found, notable zinc, uranium, molybdenum and titanium. This is unfortunate, but EMR assaying for these elements must await refinement of the NMR method on easier targets, or the development of suitable EPR methods for particular mineral deposits. All such work was assigned a rather low priority for the present.

Some of the favorable elements listed in table 3 are not mined to any extent in the United States, such as cobalt and niobium. For abundant elements such as hydrogen and sodium, no specific need for assaying is apparent. Some of the others occur in most of their ores at low concentrations, for example vanadium, copper, cobalt, cadmium, bismuth, arsenic and beryllium, so are not favorable elements for early assay logging attempts. The remainder may or may not be favorable, depending on the ore concentrations and exploration problems in particular mining districts. Two books* were found helpful in the effort to define these matters in a preliminary way. We also inquired by telephone of several government specialists in particular mineral products at the U. S. Bureau of Mines in Washington, and of the chief geologists of

*Kesler, S. E., 1976, Our Finite Mineral Resources, New York, McGraw-Hill.

*Bateman, A. M., 1950, Economic Mineral Deposits, Wiley, New York.

Table 3. The best commercial elements for NMR assay

Element	Isotope	10 kG Larmor frequency, MHz	Isotopic abundance, %	Q	Concentration in ore, %	Origin
H	1	42.57	99	0	80	All areas
F	19	40.06	100	0	<20	N.M., Mex.
P	31	17.23	100	0	60	Fla., N.C.
Li	7	16.54	93	-.04	20	N.C., other
B	11	13.66	81	.035	60	Cal., other
Na	23	11.26	100	.1	50	La., other
V	51	11.19	99	.3	1	Colo., other
Al	27	11.09	100	.15	60	Ark., tropics
Mn	55	10.55	100	.5	50	Australia, U.S.
Nb	93	10.40	100	-.2	<1	Canada, U.S.
Co	59	10.10	100	.5	1	Morocco, U.S.
Cu	63*	11.28	70	-.15	1	Ariz., other
As	75	7.29	100	.3	<1	U.S., other
Bi	209	6.84	100	-.4	1	Australia, U.S.
Sb	121	10.19	57	-.53	to 40	Ida., Mont.
Be	9	5.98	100	.02	<1	Utah
Pb	207	8.89	22	0	<60	Mo., other
Sn	119*	15.87	8	0	<10	Asia, Colo.
Hg	199	7.61	16	0	<20	Spain, Nev.
Cd	113*	9.44	12	0	1	Idaho

*The better of two good isotopes.

Table 4. Commercially desirable elements, of poor NMR detectability

Element	Isotope	10 kG Larmor frequency, MHz	Isotopic abundance, %	Q
C	13	10.7	1.1	0
N	14	3.07	99	.07
O	17	5.77	.041	.004
Mg	25	2.60	10	-
Si	29	8.46	4.7	-
S	33	3.26	0.74	.06
Cl	37	3.47	25	-.06
K	39	1.98	93	.14
Ca	43	2.86	.15	-
Ti	47*	2.40	7	-
Cr	53	2.40	9.5	-
Zn	67	2.66	4	.18
Ga	69	10.22	60	.23
Ge	73	1.48	7.7	-.2
Se	77	8.13	7.5	0
Br	81*	11.5	49	.28
Rb	85	4.11	72	.31
Sr	87	1.85	6.9	-
Y	89	2.08	100	0
Zr	91	3.95	11	-
Mo	97*	2.83	9.5	-
Ru	101*	2.1	17	-
Rh	103	1.34	100	-
Pd	105	1.74	22	-
Ag	109*	1.98	48	0
In	113	9.31	4.2	1.14
Te	125	13.45	7	0
Cs	133	5.58	100	-.003
Ba	137	4.73	11.2	-
La	139	6.01	100	.6
Hf	177	1.3	18	3.

*The better of two good isotopes.

Table 4 (Continued)

Element	Isotope	10 kG Larmor frequency, MHz	Isotopic abundance, %	Q
Ta	181	4.6	100	6.
W	183	1.75	14	0
Re	187	9.68	64	2.6
Os	189	3.30	16	2.0
Ir	193*	0.86	62	1.0
Pt	195	9.15	34	0
Au	197	0.695	100	.56
Tl	205	24.5	70	0
U	235	1.1	0.7	4.0

*The better of two good isotopes.

a number of mining companies. From this information, the following tentative conclusions were drawn regarding some of the elements in table 3:

(1) Fluorine (fluorite ore) - Favorable. Good NMR signals already demonstrated. Need for an exploration assay-logging tool has been expressed by one geologist concerned. U. S. production small.

(2) Phosphorus (phosphate ores) - Very favorable prospect. NMR assays already successful abroad. Very large U. S. production. Great interest in a borehole assay tool expressed by two Florida phosphate mine geologists. A geologist at a major North Carolina mine said they do not need assay logging; uranium correlates well with phosphorus in their deposit, and simple gamma-logging is satisfactory. This is not true of Florida ores or Idaho ores.

(3) Aluminum (bauxite and kaolin) - Favorable, except for quadrupole effect. One large bauxite mine in Arkansas "has no need for assay logging" because the ore was blocked out years ago by pattern drilling. Two other mines not canvassed. Need for an assay logging tool expressed by geologist at a Georgia kaolin/bauxite mine.

(4) Copper (many minerals) - Moderately hopeful outlook for simple-sulfide vein deposits, as at the large Butte, Montana and Sunshine, Idaho mines. Interest in borehole assaying expressed by geologists at both mines. Outlook for disseminated (porphyry) deposits not good: concentration of copper is low and the principal ore mineral, chalcopyrite ($FeCuS_2$), may not give NMR signals.

(5) Lead (galena) - Moderate outlook. Large United States production accompanied by zinc and other metals. NMR signals from galena not yet demonstrated. Two Missouri mine geologists have indicated that assay logging may be unnecessary since cores are required anyway to define facies relations. Utah mine geologist has expressed interest in assay logging.

(6) Antimony (stibnite) - Outlook good. United States mines are small, but ore grade is erratic. Drilling and assay are used to guide mining and leave waste. President of the largest mine, in Montana, is enthusiastic about borehole assays. Ore runs up to 40% antimony, averages 2.4% at present.

(7) Vanadium - Outlook mostly unfavorable. Geologists at mines in Utah and Arkansas badly need an assay logger, but average ore grades are so low that it will be difficult.

(8) Lithium (spodumene in pegmatites) - Outlook moderately favorable. Coring is customary at North Carolina mines, ore runs only 1.5% lithium average, but large spodumene crystals contain 20%.

(9) Boron (several borates) - Outlook borderline. California mine geologists prefer to core for information on geology, sodium and calcium content as well as boron. Assay logging may be useful in wildcat prospecting, but all hard white minerals found can be assayed at low cost already.

(10) Beryllium (bertrandite) - Unfavorable. Utah clay ore contains only 0.7% BeO equivalent, though otherwise an assay logger might be helpful.

(11) Rare earths (monazite sand or bastnaesite) - Mostly unfavorable. Although six of the rare-earth metals give fair NMR signals, cerium, which is the principal metal, gives none. The monazite sand in which they occur constitutes only 1% of the old beach deposits being mined in Georgia and Florida. However, there may be application of NMR assaying in the ore beneficiation, where 8 valuable heavy minerals are concentrated and sorted. The world's largest rare-earth mine, in California, has much richer ore, averaging 12% CeO equivalent, but they must core anyway to get mineralogical information for ore dressing.

The tentative evaluations given above must be regarded with caution. Conditions and practices at different mines differ radically, and inquiries could greatly change the conclusions. Also, conditions change and people learn. It is likely that as assay methods develop and are demonstrated, geologists may see ways of applying them to advantage where they now see none. We decided to concentrate now on the most promising elements and industries but leave open the option to consider others later. The most promising materials for assay logging were concluded to be Florida phosphates, fluorspar, bauxite, certain vein copper sulfides, galena, and stibnite.

4.2 VISITS TO MINES AND ORE-PROCESSING PLANTS

Early in the program, in the course of a trip to Utah, valuable contacts were made with three mining companies in Salt Lake City and with several EMR specialists at the University of Utah. Large samples of four U. S. ores were obtained for use in lab tests and in building borehole models, from Anaconda, ASARCO and Kennecott, as follows:

100 lb of 9% to 20%, crushed, Nevada fluorite (in feldspar).

50 lb of Park City galena/sphalerite chunks (with quartz).

50 lb of Bingham mine ore with 0.5% copper.

5 lb of Bingham chalcopyrite concentrate powder (equivalent to 500 lb of mine-run ore).

1 lb of analyzed concentrate standards, containing molydenum, gold, silver, etc.

10 lb of mineralized cores from a copper prospect in Wisconsin.

Small samples of the fluorite ore, the galena (after crushing) and the chalcopyrite and molybdenum oxide concentrates were taken to EPR and NMR specialists at the University of Utah, with whom a consultation meeting had been held and who had expressed interest in helping in the program. Their findings will be given in section 5.

Enroute from the 6th ISMAR conference on EMR in May, in Alberta, visits to several major metal mines near Butte, Montana and Coeur d'Alene, Idaho were planned. Purposes were to collect representative ore samples and to study the constraints under which a logging-assay tool must operate. Circumstances (strikes and illness) prevented these visits, but a satisfactory visit was made to the phosphate mining operations near Soda Springs, Idaho.

The soft brown Phosphoria shale outcrops along at least 30 miles of a low mountain ridge in southeastern Idaho. It is being surface-mined by several companies, and there are four major phosphate processing plants in the area, together capable of handling about 40,000 tons of ore daily, to produce fertilizer and chemicals. There are readily minable reserves for at least 30 years. Contacts were made with the Monsanto, FMC, Simplot and Beker companies. The Beker mine was visited and ore samples containing 15% phosphorus by weight were obtained from the richest bed. The senior geologist there was enthusiastic about the prospect of an assay logging tool for their 5-inch exploration holes. At present, up to 100 bags of drill samples are caught from each hole, and are analyzed by wet chemistry, with usual delays of up to 9 months! Beker also needs a surface tool to assay flat ore faces as they are exposed by stripping. The site geologist now guides the excavating by ore color, backed up by a few 1-day chemical analyses. This is not accurate because color is also affected by variations in the organic carbon and in the iron oxide present. Radioactivity measurements have failed to correlate with phosphate and have been abandoned (despite the reliance on them expressed by a geologist at Simplot).

It was learned that quick assays of process streams are satisfactorily done at the FMC plant by X-ray fluorescence. It is not known to what extent this method is used elsewhere. In any case, it does not appear to be adaptable to field use.

Visits were also made to a number of mines in the Southeast, for the same purposes. The minerals involved, and principal findings, were as follows:

(1) Phosphates: Several counties of central Florida are underlain by a 6-foot phosphate-rich bed of dark, soft "matrix" just above limestone bedrock, covered with some 30 feet of gray clay and 3 feet of surface peat. Stripping is done with bulldozers followed by giant draglines. The ore contains 2.5 to 6% of elemental phosphorus by weight, and the grade is tripled by mechanical sorting, washing, and flotation (of the fines). There are at least a half-dozen large surface mines and processing plants (many with enormous, million-ton, outdoor product stockpiles), which together can produce 100,000 tons of concentrate daily. About half of this is exported for the fertilizer essential to feed mankind.

At the Agrico mine and plant near Mulberry, Florida, minability is determined by the thickness ratio of matrix to overburden in relation to the current price of the product. Grade is predicted from "cookie cutter" coreholing to 50 feet on a 330 foot grid at a cost of $400 per hole including $100 for wet chemical analysis. A phosphorus log alone (it is said) would be adequate for grade determination on prospect areas to be considered for purchase. The 4-inch holes are water-filled, but generally could be re-entered by a logging tool, mounted on the end of a drillstem or a plastic pipe to prevent caving

of the soft formations. Several Florida phosphate geologists have expressed interest in an assay tool.

In the Florida plants, instrumentation is not used effectively. Automation of process control has been attempted, but intermittent, inaccurate human control is the rule. Gamma ray density gauges are used on the product streams. There may be applications for continuous - assay instrumentation, if plant efficiency ever becomes important enough to the management.

(2) Bauxite: In Arkansas, very large alumina plants are operated by the Reynolds Metals Co. and by Alcoa. These plants, plus a small American Cyanamide ore-treatment plant, were visited briefly. Each receives its hard, gray, pebbly, oölitic bauxite ore from a large open-pit mine nearby. A Reynolds geologist expressed a need for a direct analytical tool to supplement wet chemistry. Their analytical laboratory is frequently overloaded. They need 2% accuracy. Unfortunately, in addition to aluminum, they need analyses for Na, OH, CO_3 and Si to determine the ore grade. This is not likely to be possible by NMR.

A small need for borehole and mine-face assays exists at the kaolin/bauxite mines of C&G Chemicals and of American Cyanamide near Andersonville, Georgia. Pods of bauxite, a premium material, are found in the thick kaolin bed. Both are gray to red, and are now distinguished by a chewing test: kaolin is soft, but bauxite is gritty. An NMR log should be capable of distinguishing these ores (see section 5).

(3) Rare Earths: In Northeastern Florida, some 30 square miles of a Quaternary heavy-sands ore body lies beneath swamp, forest and 10 feet or more of barren sand. This is being mined and beneficiated by three companies, using efficient, large-scale, all-hydraulic methods like those used worldwide.

The body of ore-grade material (above 2% heavy minerals) has been outlined approximately by auger drilling, with hydraulic separation of heavy fractions and optical analysis. The latter, consisting of the recognition and counting of eight types of mineral grains under the mineralogist's microscope, is also used hourly to grade the process streams in the large, new, dry-separation plant of the Titanium Enterprises Company. An accuracy of 0.1% is said to be achieved in 30 minutes per sample. X-ray fluorescence may be installed later as an analytical method, but they will welcome alternative techniques for continuous use in the process streams.

Borehole logging is considered impossible because the holes frequently collapse when the auger is withdrawn. It is also discouraged by the low grade of the ore. The most valuable minerals produced are monazite, rutile, and zircon, containing the NMR - responsive elements La-139, Ti-47, and Zr-91, respectively. Gamma-ray density gauges are used to integrate the flow of products on conveyor belts. Excellent samples of the products were obtained for study. These minerals are not considered prime candidates for EMR assaying, but may be good secondary prospects.

(4) Spodumene (lithium): Near Kings Mountain, N.C., there are several dozen large, vertical pegmatite pods which are being open-pit mined by the Lithium Corp. of America and by Foote Minerals. We visited the latter briefly and obtained samples. They produce, in addition to spodumene: mica, beryl, tourmaline, and glass sand. They sell the amphibolite country-rock waste, presumably as concrete aggregates and road metal. Their plant is considered secret because of the competition, but it is known that the separation process used is foam flotation. Since lithium gives a good NMR signal, it is likely that an assay logging tool could be useful in this industry.

(5) Mid-Continent Lead/Zinc: The most important U.S. source of lead and zinc is the new district near Viburnum, Missouri where several major underground mines are located. A detailed sampling visit and discussion were made to the well-kept Brushy Creek mine of the St. Joe Mining Co. The ore minerals galena, sphalerite and chalcopyrite occur in veinlets and vugs in varying ratios, irregularly distributed within a 20-foot thick brown dolomite bed at a depth of several hundred feet. Exploration drilling from the surface takes size AW, 1-inch cores for stratigraphy as well as ore grade, to a depth greater than 1000 feet. I learned that some years ago, the Schlumberger Company (working at this mine) developed a fairly successful borehole assay method (principle not known), but St. Joe Mining decided they didn't need it.

Underground practice is not to mine ore selectively according to grade, but to mine the whole 20-foot bed in a room-and-pillar pattern. Everything is ground up fine and the metallic minerals are removed by flotation. This practice seems to be dictated by the erratic distribution of ore in the rock. Average mill feed grade is only 1% lead/zinc, but groups of veinlets would assay 10% to 50%, by their appearance.

An automatic X-ray fluorescence analyzer handling seven process streams was observed in action at this plant. It determines the concentrations of three metals and total solids in a water slurry to 0.5% precision every 7 minutes, printing out the results on a strip of paper. The instrument operates reliably 90% of the time; the chief problems arise from clogging of the plastic slurry-feed tubes. Such equipment, made by Applied Research Labs (and by Outokumpu Oy in Finland) is said to be in use at a majority of the large Missouri lead-zinc mines.

These findings all tend to discourage the development of EMR logging and assay tools for lead/zinc.

(6) Vanadium: The large Union Carbide vanadium mine at Wilson Springs, Arkansas, exploits a clay ore from an open-pit excavation. Ore grade varies from 1 to 2%. In sorting ore from waste at the mine (a truck-load at a time), they attempt to estimate grade by a gamma-ray (fluorescence?) test, which is not reliable. They would like a better assay method. The expected weak NMR signal of vanadium, and the low concentration of the Arkansas ore as well as that of Colorado and Utah make the prospect of initial success small for vanadium.

In addition to the mineral samples obtained through direct visits, many more were received by mail, package-service or freight as a result of telephone

or letter contacts. These were as follows:

(a) 75 lb of Florida phosphate cores, from International Minerals and Chemical Corp.

(b) Some North Carolina phosphate ores and concentrates, from Texas Gulf, Inc.

(c) 30 lb of Minnesota manganese ore and concentrate, from the Hannah Mining Co.

(d) Butte, Montana rhodochrosite (pink manganese ore) from the Anaconda Co.

(e) Butte, Montana chalcocite and blue covellite, copper sulfide ores, from the Anaconda Co.

(f) Idaho tetrahedrite copper/antimony/silver ore from Sunshine Mining Corp.

(g) Utah/Colorado vanadium ore and refined oxides, from the Atlas Minerals Co. and from Union Carbide.

(h) Montana stibnite ore from the U. S. Antimony Co.

(i) Colorado molybdenite ore from the Climax Molybdenum Co.

(j) California bastnaesite (rare earths) 7% ore and leached concentrate, from Molycorp, Inc.

(k) Utah clay beryllium ore, from Brush-Wellman.

Depending on the concentration and Larmor frequency of the commercial element, each of these ores has been subjected to an NMR test, or has been submitted for ENDOR testing, as detailed in the next section of this report.

4.3 LABORATORY TESTS ON MINERAL SAMPLES

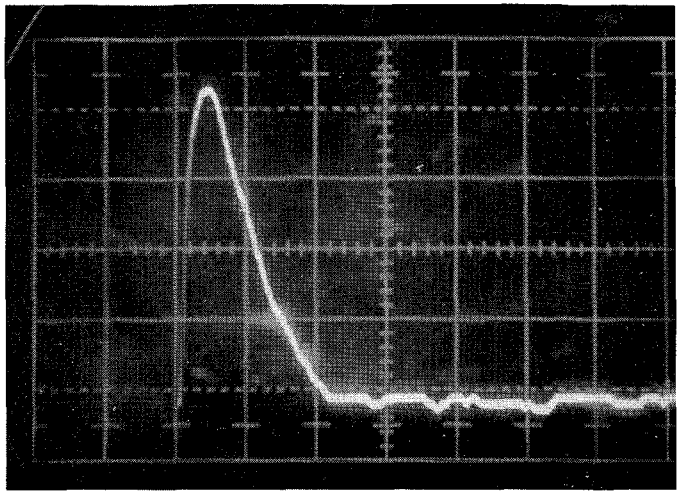
An important part of determining whether NMR assay logging may be feasible is, to find out whether natural ores, with all their impurities and crystal imperfections, will allow the resonances of the nuclei of interest to be detected. It was especially important in this program to do this for U. S. ores. There is very little published NMR data on natural minerals, and essentially all of it is for minerals in other countries. There is reason to believe that every mineral locality will be enough different from every other in chemistry and mineralogy, that the NMR response of an element of interest cannot be predicted. Hence, tests are essential.

The first tests were made by consultants at the University of Utah, who also offered various useful suggestions on our problem. Dr. David Ailion, well-known for his NMR studies of fluorite, was contacted initially because of his papers on a "zero effective field" technique. Dr. Ailion advised

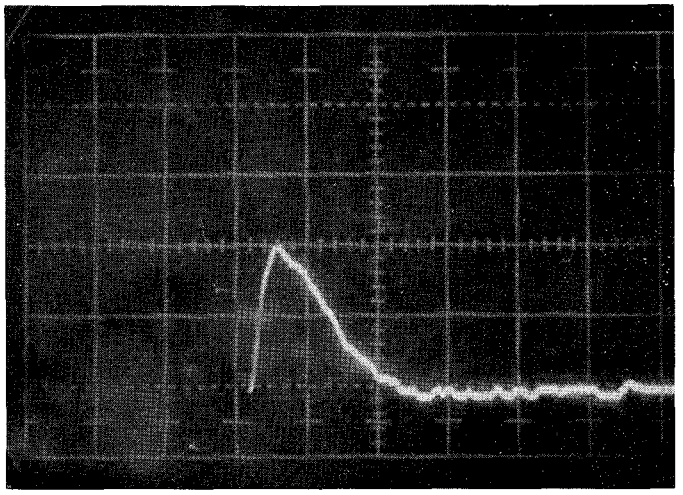
that the molybdenum nuclear resonance could not be reached with U. of U. equipment, and that the two copper resonance lines from chalcopyrite (Cu Fe S_2) might be spoiled by the strong local magnetic field (up to 100 kG) from the iron atom within each chalcopyrite unit cell. However, he expected to see the lead in galena after retuning of the spectrometer (a difficult process). He readily obtained the fluorine signal from the fluorite ore sample, as shown in figure 22, and determined the relaxation time T_1 to be 17 seconds. To test the fluorite ore, he used a pulse technique yielding a spin-decay signal which is the Fourier transform of the spectral line. Figure 22a is the spin-decay from a sample of pure (synthetic) fluorite powder. Figure 22b is that from an equal sample of the ore, purported to be 20% fluorite by volume. The horizontal scales in figure 22 are all 12 microseconds/cm and the apparent transverse relaxation time T_2^* for this material is about 15 microseconds. From the relative areas of a and b, it appears that the ore is about 40% fluorite. Figure 22c is for 1/5 of the ore sample, diluted with inert NH_4Cl, at double the vertical gain of photos A and B. A zero baseline produced with the magnet detuned is shown for comparison. The fluorine signal is well above noise and would permit an estimate that the diluted ore is 8% fluorite, which is near the lower economic limit for this ore. Hence it can be concluded from this, the first NMR test performed under the program, that natural Nevada fluorite ore can readily be assayed for its fluorine content by spin-decay NMR. This agrees with published foreign results.

Dr. William D. Ohlsen, of the University of Utah, who is well-known for his EPR studies of rutile, advised the application of a zero-field (NQR) method to our problem, employing an untuned (traveling wave?) technique he had heard of, used in Sweden. (A reference on this technique which he gave proved disappointing, however.)

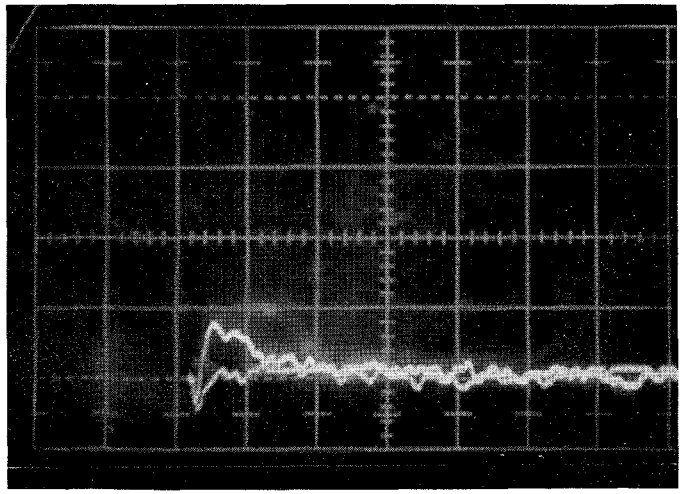
Figure 23 presents EPR spectra of four ores tested for us by Dr. Ohlsen. These spectra are all different and might be considered capable of identifying the minerals, except that the 6-line patterns are probably all caused by manganese impurity, according to Dr. Ohlsen, and manganese occurs as an impurity in nearly all colored and opaque minerals. The additional structure in the molybdenite (MoS) and fluorite (CaF_2) spectra is thought to result from magnetic interaction between the manganese and other magnetic particles (molybdenum and fluorine nuclei, perhaps), so might be used as a diagnostic "fingerprint". The extremely broad response seen for the chalcopyrite ($CuFeS_2$) indicates that a very large amount of magnetic material is present; this no doubt is caused by the iron atoms present in every unit cell. Since both of the concentrate samples contain pyrite (FeS_2) crystals also, some of the broad response may be caused by pyrite, which is not considered worth mining for its own sake, as a rule. Thus A. S. Marfunin's published implication that EPR signals do not directly identify or tell the amounts of major minerals present seems to be true. Considering also the very great breadth of the EPR lines, (e.g., ~ 1000 gauss for the manganese patterns) it is hard to see how this type of EMR spectroscopy could be adapted to low-field measurements in the rock outside of a borehole.



A.



B.



C.

A. (Upper left) - Pure fluorite standard.

B. (Upper right) - "20%" Nevada fluorite ore.

C. (Lower left) - "4%" Nevada fluorite ore mixture, at double gain, with detuned reference baseline.

NOTE: All horizontal scales = 12 μsec/ large div.

Figure 22. Fluorine-19 spin-decay NMR signals

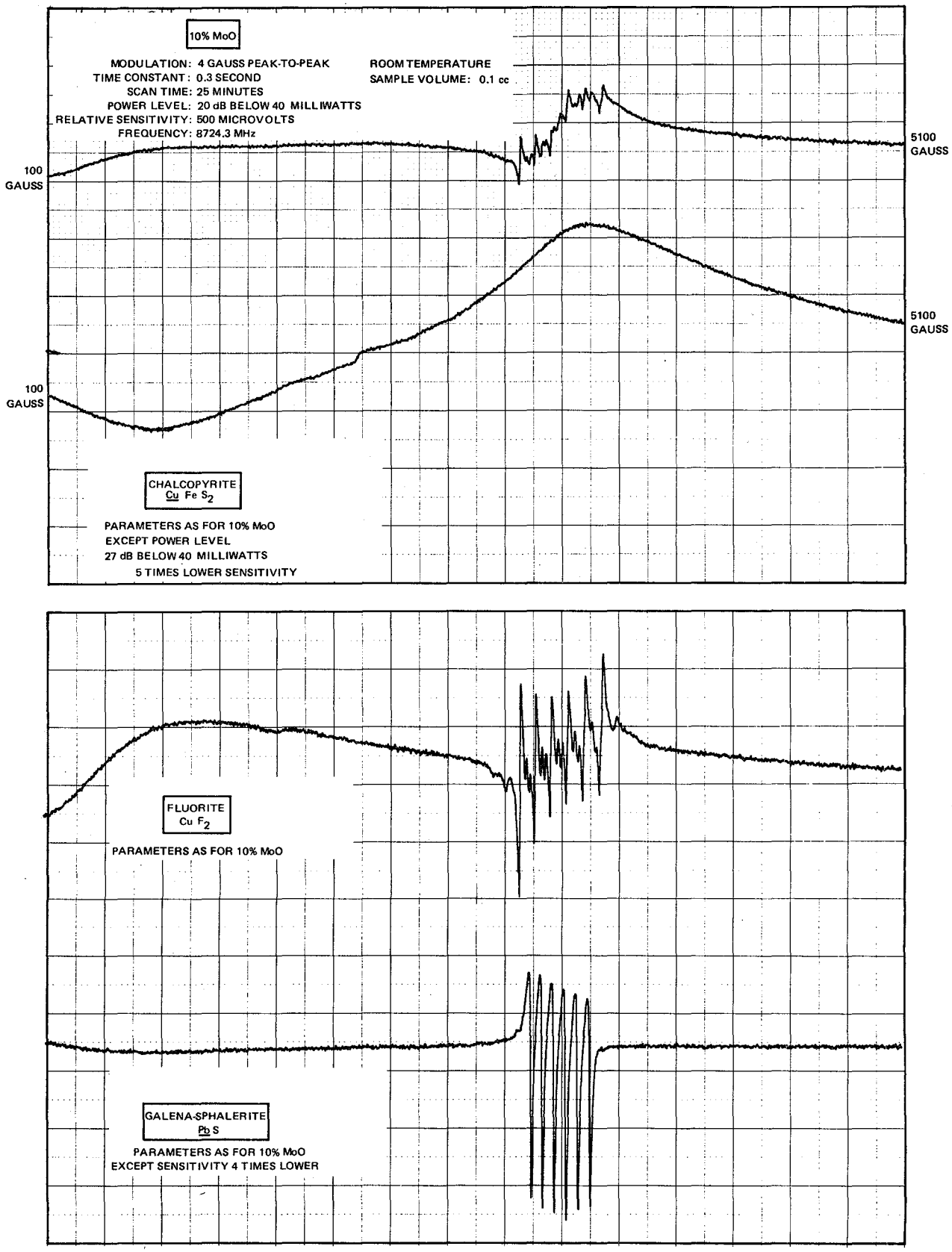


Figure 23. EPR spectra of four ores: Molybdenum concentrate, chalcopyrite concentrate, 20% fluorite, and galena/sphalerite

G 9474

Several NMR tests were run on crushed samples of chalcopyrite (CuFeS) and galena (PbS) in the pulse spectrometer at North Texas State University (NTSU), with the aid of Dr. Ray Sears of that institution. The equipment included a 15 kilogauss (kG) magnet), a 1 kW pulse generator and an rf receiver operating at 14 MHz, a "boxcar" integrator, oscilloscope and strip-chart recorder. Dr. Sears had set the equipment for the stronger of the two copper resonances, and believed that he was seeing a signal from the copper coil in the sample head itself. Figure 24 shows this signal, recorded with no sample in the holder, at a slow scan rate of 5 gauss/min. Immediately after this record was made, the sample tube was filled with chalcopyrite concentrate powder and the scan was repeated. Each recording required over an hour to make. There was no significant difference between the two recordings when they were superimposed on a light table. If figure 24 is indeed a signal from copper, this means that the chalcopyrite does not produce a copper NMR signal, possibly because of the magnetic disturbances of the iron atoms.* If true, this conclusion has serious negative consequences for borehole assaying, since chalcopyrite is the most important copper mineral. We hoped to check this result on more powerful equipment using bigger samples, and on solid ore that has not been stressed by grinding.

Dr. Sears also tuned his equipment for lead (although some parameters could only be estimated) and we ran 2-hour scans at the maximum feasible sensitivity on both galena and lead fluoride samples. No signal whatever was seen. To get the equipment into optimum adjustment for solid compounds of lead may require several days, because the T_1 and T_2 are unknown. Both Dr. Sears, and Dr. Ailion (of the University of Utah) considered lead a promising element for NMR, so further tests were planned for galena. It must be remembered that the NMR - responsive isotope of lead, Pb-207, constitutes only 22% of all the lead in natural samples. This will result in a correspondingly weaker signal.

Numerous institutions engaged in NMR in Texas and surrounding states were canvassed by telephone to locate equipment more powerful than that at NTSU. Three possibilities were found. After considerable negotiation, arrangements were made for a short experiment at the Mobil Research Labs in Dallas. This private industrial laboratory has a 23.5 kG magnet and high-power pulse equipment capable of operation at 50, 25, and 8 MHz with an integrator, capable of detecting essentially all of the isotopes of interest to us. The operator, Dr. Donald Woessner, a physical chemist, has obtained a sodium signal from only 1 milligram of NaCl, and a strong copper signal from his coil. He now uses a silver coil to measure copper. With this coil, a number of copper and other resonances were successfully measured, using a strong field, and the stacking of 100 pulses. A 2.5 ml sample, consisting of the mineral diluted with sugar as indicated in table 5, was used.

*According to R. T. Schuey in Semiconducting Ore Minerals, Elsevier Pub. Co., Amsterdam, 1975, chalcopyrite is antiferromagnetic. The iron atoms are arranged in layers of opposite polarity alternating with copper atoms, and the iron fields cancel to zero at the copper positions. This however assumes no distortion of the lattice.

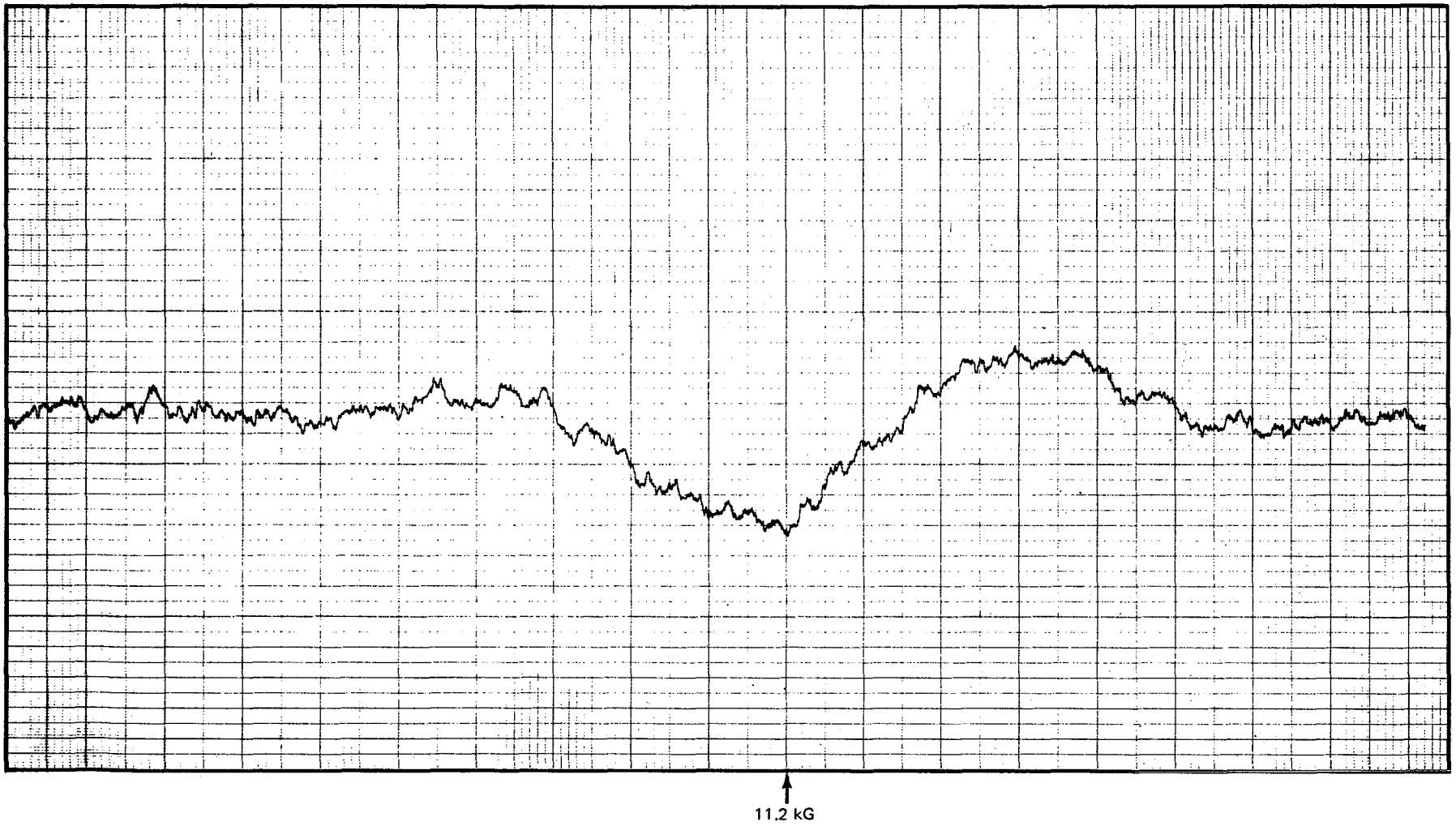


Figure 24. A copper (?) NMR spectrogram; horiz. scale, 50 gauss/large div. = 1 minute of time. Pulsing rate, 10/sec, 14 MHz. Envelope filter time constant = 0.03 second.

G 9475

Table 5. NMR tests at Mobil

Sample	Signal,mV	Baseline,mV	T_1,ms	T_2^*,ms	Other
Cu filings, 10%	+618 ±3	+3	~1000	~150	
Chalcocite, 50%	±1.5 ±3.7	-17.±2			
Chalcocite, 50%	-8.0 ±3	-13 ±2.5	<1000?		6 pulses/min
Covellite, 33%	-211 ±3.3	+0.3 ±0.7	<1000?		6 pulses/min?
No sample	-	-8.4 ±2.4			
No pulse	-	-7.7 ±2.5			
Covellite, 33%	-24 ±0.7	-6.1 ±2.9			
Chalcopyrite, 50%	-15.2 ±1.3	-14.0 ±0.8			
Chalcopyrite/rock	-3.4 ±1.7	-16.8 ±1.4			
CuCl, Powder, 10%	+595.6	-1.	5.8	0.125	
Fla. Pebble Phosphate	+2,478 ±25	-	~230	~0.20	
Spodumene, 10% (for Li)	+716 ±1	-	42	0.08	

In a magnetic field adjusted for optimum response to a sample of copper filings, the silver sample coil was energized with a 4-microsecond pulse (found to be the optimum, "90 degree" length) of 26.45 MHz RF energy. After a 45-microsecond delay to allow for the decay of transients, the pulse-decay tail was sampled for 10 microseconds. The sequence was repeated no more often than once per second to allow re-alignment of the nuclei by the 23.4 kG magnetic field. After 100 pulses, the sample sum was printed out on a paper tape. Estimates were made of T_1 by noting the decrease of signal with increased repetition rate, and of T_2^* by the shape of the decay tail, wherever the signals were strong enough to be seen on an oscilloscope. All results are presented in table 5.

It can be seen that all three natural copper minerals gave a much weaker signal than either diluted copper filings, or copper chloride power. Also, the ore signals may be either positive or negative with respect to the base line (a phase-sensitive detector was used). The weakness of these signals has since discouraged further work on copper. However, Dr. Woessner of Mobil was intrigued by them and discussed them with colleagues at a professional meeting. The result was a hypothesis that because of quadrupole

splitting in the sulfides, the spin-3/2 copper nucleus was giving only a ±1/2 spin transition signal, for which our "90-degree pulse" became a 180° pulse; this would give a signal near zero, which could vary from plus to minus with slight drifting of the excitation pulse height or length. Apparently, the experiment with copper ores should have been repeated, using a pulse half as long.

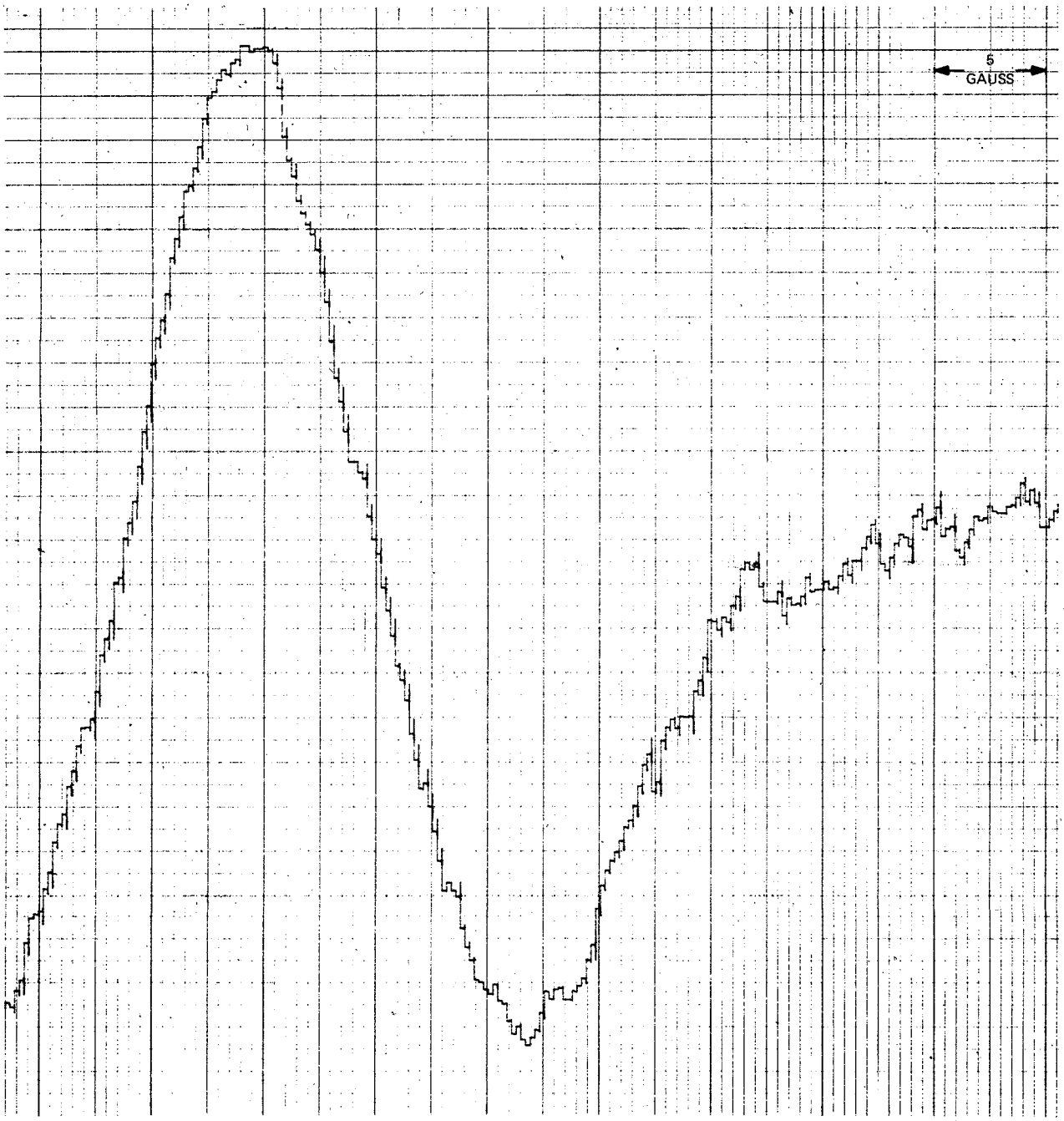
The Florida pebble phosphate, which constitutes the coarsest fraction (about 1/3) of the Florida ore, gave an excellent signal, and apparent values of decay times T_1 and T_2^* that appear to be amenable to assay logging using Professor Béné's switched-field methods. The same was true of spodumene (lithium) ore from North Carolina, but to a lesser degree. The apparent values T_2^* are doubtless shorter than the true spin-spin relaxation times of the materials, because of inhomogeniety of the strong field H. These results were therefore quite encouraging.

Subsequently, two additional series of conventional NMR tests were performed in the strong-field, RF-pulse spectrometer at North Texas State University, with the help of Prof. Ray Sears. There were two objectives: to test the new ores obtained, and to retest the copper ores with half-size pulses to check out the above hypothesis for the failure of the tests at Mobil.

With regard to this hypothesis, Prof. Sears immediately explained that it would not apply to a spectrum of the sample such as he takes with his equipment. Even if the pulse which is optimum (90°) for metallic copper (filings) became 180° for copper sulfides because of quadrupole splitting, some signal would be seen when off-tune, because in the rotating frame a composite field strength is seen by the sample, which is a resultant of the RF peak amplitude and a portion of the dc aligning field (which portion becomes zero at resonance). At some off-resonance dc field value, this would give a highly effective 270° pulse. Hence, a spectrum cannot fail to show any resonances present. Prof. Sears demonstrated this by using a pulse duration of twice the optimum length for the sodium in a sample of NaCl.

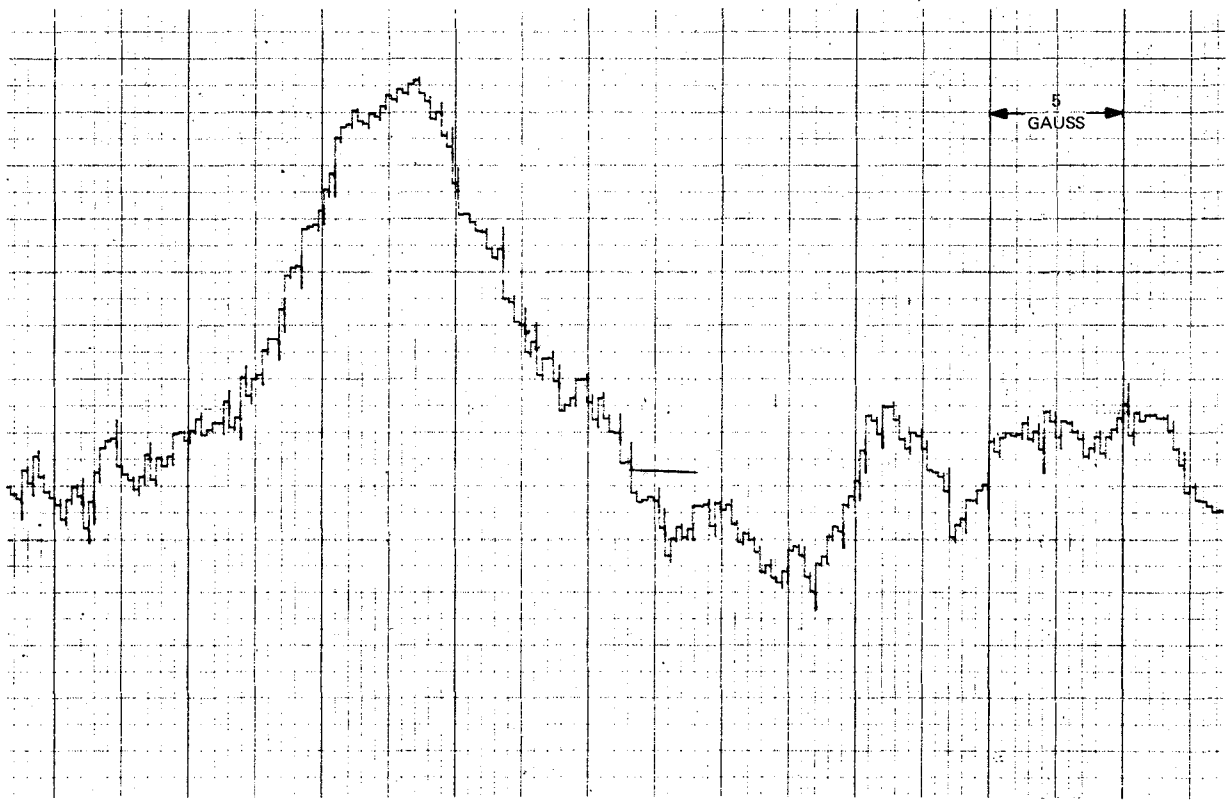
We proceeded to record NMR spectra for three copper ores, cupric and cuprous chloride (both with water of crystallization), and copper filings diluted with sugar 9 to 1, and other substances. The pulse height and length used were adjusted to the optimum for sodium, which is close to copper in its gyromagnetic ratio. This adjustment is not critical. From the earlier work at Mobil, and general experience with the T_1 values of solids, we chose the interval between pulses of 2.5 seconds as being probably long enough, yet permitting enough tests to be made in one day. The pulse-decay was sampled 25 microseconds after the pulse turn-off (as a best compromise), the sample level was stored by the boxcar circuit, and was plotted by the chart recorder as a function of the dc field as this was slowly swept through resonance at 5 gauss per minute. The maximum usable gain was used, and there was fairly bad zero drift with the weaker spectra.

Figures 25, 26 and 27 display the copper spectra obtained with an RF pulse of 14 megaherz. The center of the sweep was in all cases about 12,408 ±25 gauss. Table 6 lists the signal amplitudes (as nearly as these could be estimated for various gain settings) on a common basis, and other pertinent parameters of the tests.

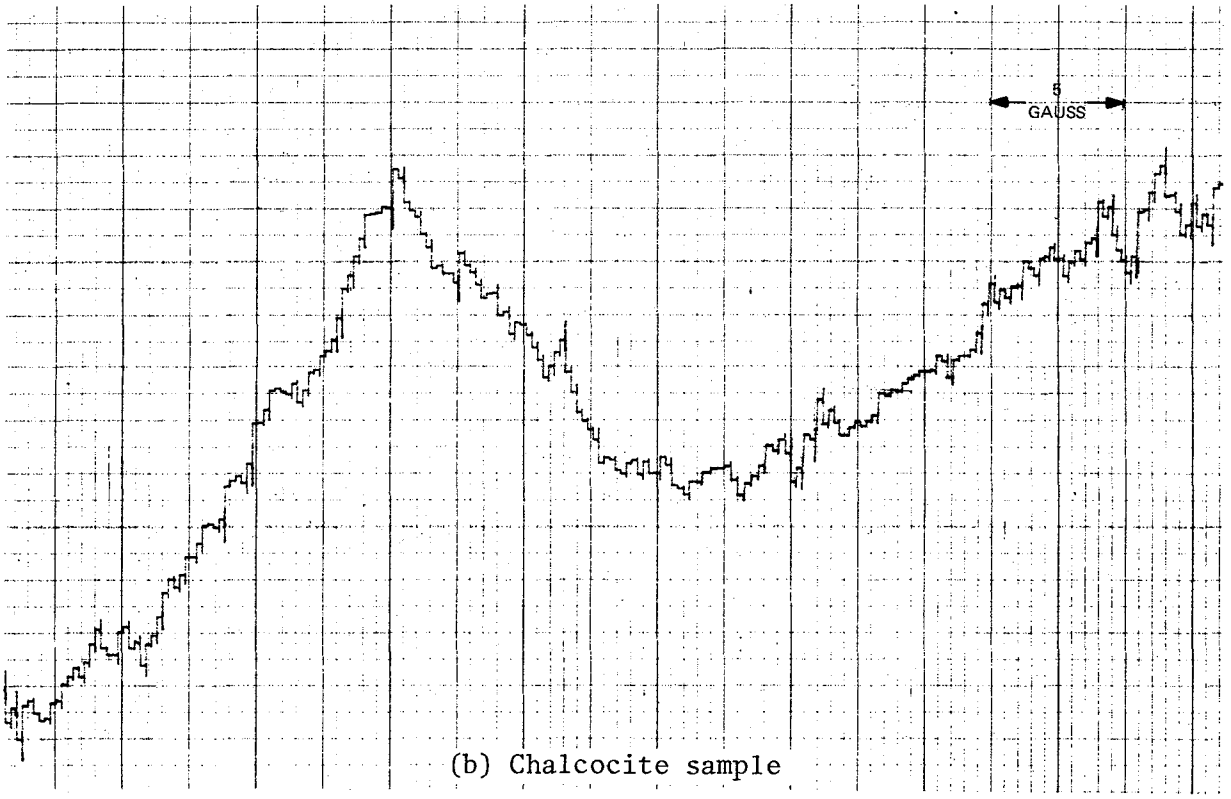


(Vertical scale chosen arbitrarily to display noise)

Figure 25. Pulse-decay NMR spectrum, with sample of 10% copper filings

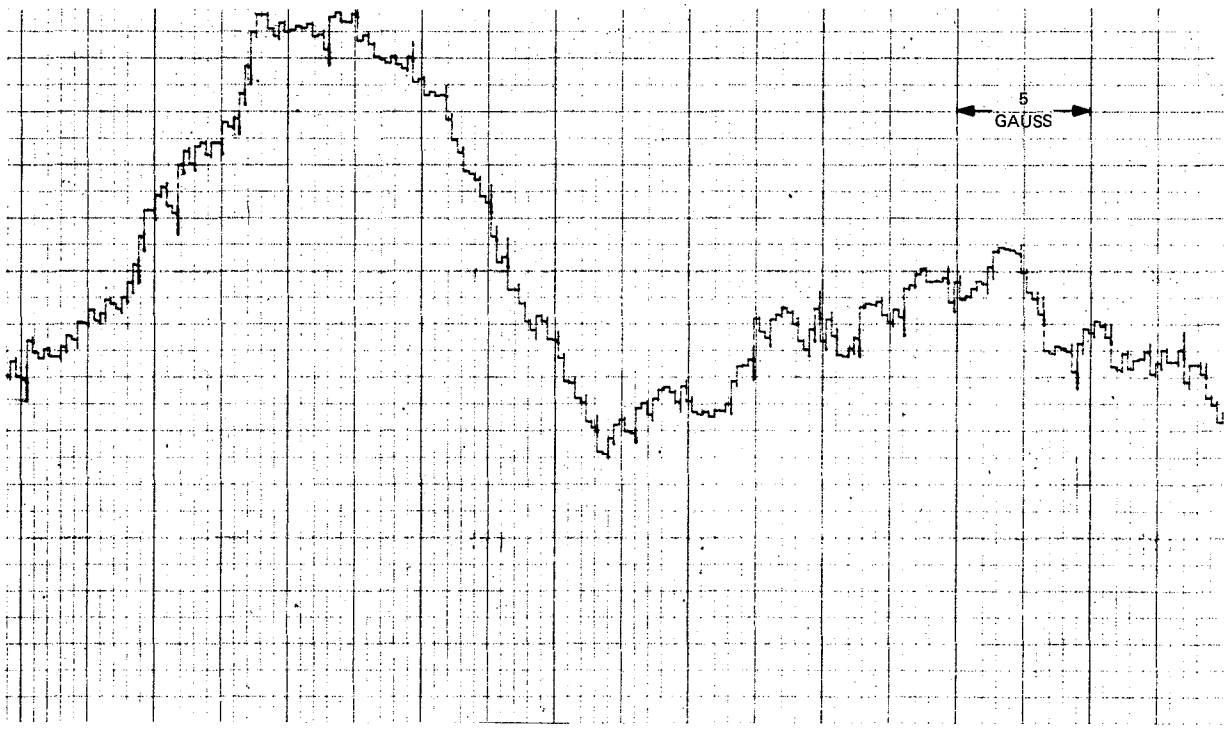


(a) No sample

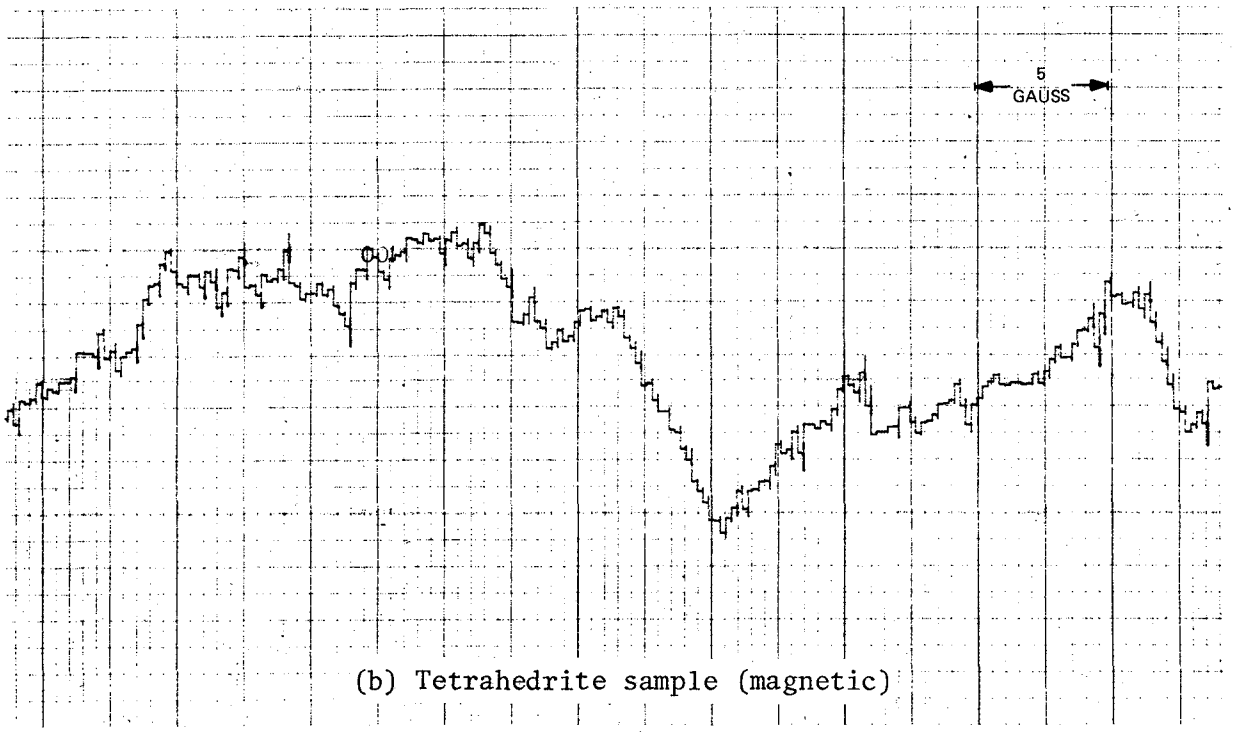


(b) Chalcocite sample

Figure 26. Pulse-decay NMR spectra for the copper coil alone (a) and with an ore (b). (arbitrary vertical scales)



(a) Covellite sample



(b) Tetrahedrite sample (magnetic)

Figure 27. Pulse-decay copper NMR spectra, two ores (arbitrary vertical scales)

Table 6. Strong-field NMR ore results

Sample	H_o	Amplitude, chart div.	Remarks
10% Cu	12,408 G	22	
Cu $Cl_2 \cdot H_2O$	12,408 G	5	
Cu Cl	12,408 G	4	
Tetrahedrite	12,408 G	5	sample very magnetic
Chalcocite	12,408 G	7	
Covellite	12,408 G	8 (?)	
Coil only	12,408 G	6 to 8	
Phosphoria (Idaho)	8,125 G	43	T_1~2 sec, T_2*~250 μsec
Al P	8,125 G	5	
Mn ore (Minnesota)	13,270 G	<3	sample slightly magnetic
Rhodochrosite (Montana)	13,270 G	<3	sample slightly magnetic

It is evident from figures 25-27 and table 6 that the Idaho phosphate ore is another excellent candidate for NMR assay logging. It is also clear that there is simply no hope for NMR assay logging for any of the important U. S. copper or manganese ores. In four instances (including chalcopyrite, tested earlier) this may well be associated with the fact that these ores are noticeably attracted to the poles of the big dc magnet, so may contain large concentrations of paramagnetic substances. The lack of any appreciable NMR signal (greater than that from the copper RF coil) from chalcocite, covellite and the hydrated copper chlorides, and the lack of any phosphorus NMR signal from aluminum phosphide, is still not fully understood.

In a third experiment at North Texas State University, several other mineral samples were tested in the pulse spectrometer with the aid of Professor Ray Sears. Various useful results were obtained.

Table 7 lists the materials tested for an easily-visible signal on the oscilloscope. The procedure was to set the pulse length for a 90° rotation of the polarization for the particular nucleus (or one of similar gyromagnetic ratio), to pulse repetitively at about 1 pulse/second, and to scan the magnetic field slowly through the calculated resonance value, at about 10 gauss per minute, while watching the oscilloscope for a pulse-decay signal with the gain high enough to see the electronic noise (which was 50 mV peak-to-peak).

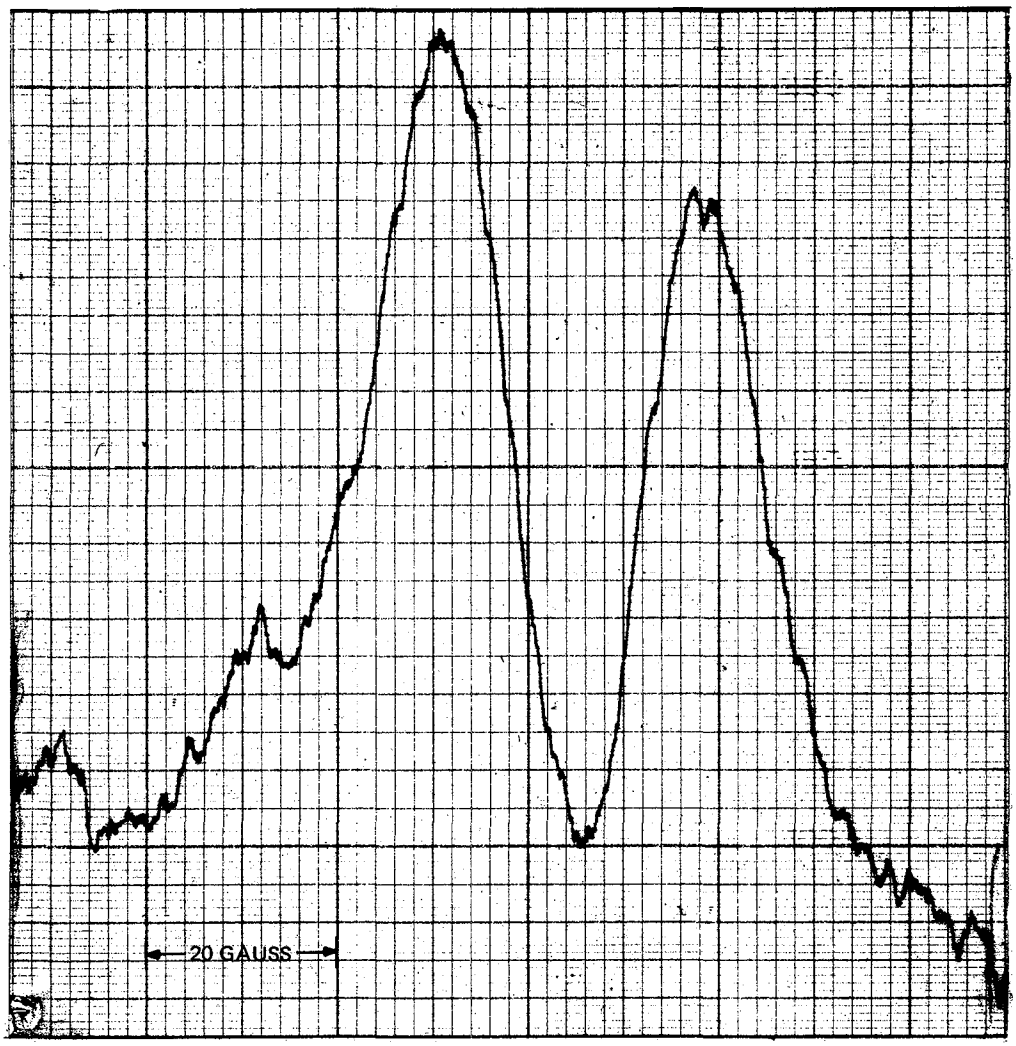
The aluminum minerals were studied further by setting the equipment for an optimum signal from $Al_2 P_3$, then using a sampling "boxcar", timed to occur during the decay tail, with a 10 Hz low-pass integrating filter and chart recorder. The magnetic field was swept at 20 gauss/minute and 20 pulses/second were applied. Figure 28 shows an aluminum spectrum obtained from wet Arkansas bauxite (dry bauxite gave an identical signal) and a kaolin spectrum at the same scale. Table 8 lists the relative signal strengths obtained from three materials. It can be seen that the spectra for bauxite and kaolin are distinctly different in shape, and should be readily distinguishable by an NRM spectrum-type logging device. It is disappointing that the signal strengths are much less than that of the synthetic material, aluminum phosphide. This may be a consequence of its greater purity. The pattern widths shown in figure 28 are about 50 gauss, that is, 55 kiloherz. Any borehole device must therefore operate at field strengths and resonance frequencies considerably greater than this, unless the lines can be narrowed by probe-spinning or multiple-pulse techniques.

Table 7. Other materials (elements) tested for NMR

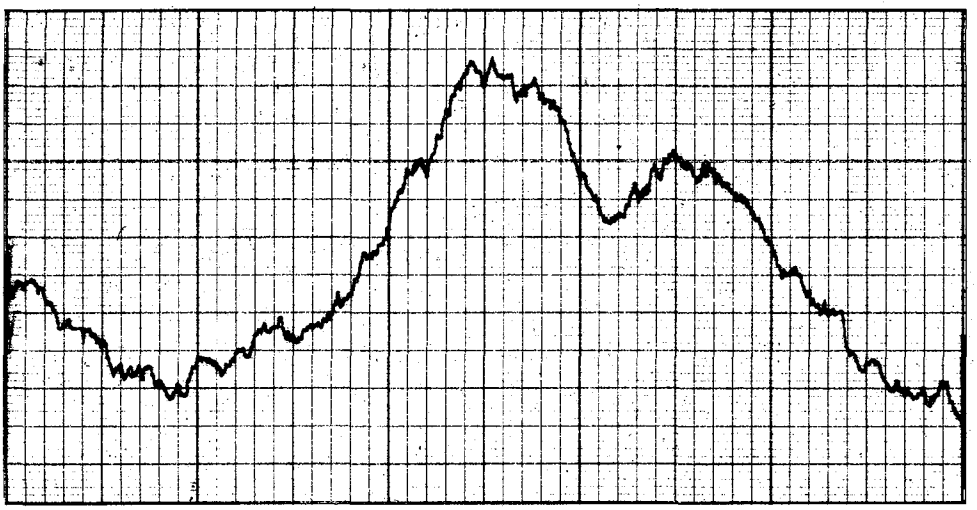
Mineral	Element	Signal mV	Est. T_1, ms	Est. T_2*, μs
$Al_2 P_3$	P	50		
$Al_2 P_3$	Al	200	10	50
Fla. concentrate	P	50	400	200
N.C. concentrate	P	50	400	200
N.C. spodumene	Li	150	60	200
Colo. green-cake	V	200	0.03	30
N.C. spodumene	Al	-	-	-
Ark. bauxite	Al	-	-	-
Ga. kaolin	Al	-	-	-
Mont. stibnite	Sb	-	-	-
Minn. ore	Mn	-	-	-
Borax	B	-	-	-
Utah galena	Pb	-	-	-

Table 8. Aluminum NMR signals

Material	Amplitude	Est. T_1	Est. T_2*
Aluminum phosphide	23 div.	10 ms	50 μs
Arkansas bauxite	1 div.	50 ms	18 μs?
Georgia kaolin	0.4 div.	- -	18 μs?



(a)



(b)

Figure 28. NMR spectra of Al in bauxite (a) and kaolin (b) (arbitrary vertical scales)

G 9758

In summary, at least some NMR testing has been done on samples of 18 important U.S. ore minerals. Ores of phosphorous, aluminum, lithium, fluorine and vanadium gave good NMR signals at distinctive values of the polarizing magnetic field (for a given Larmor frequency). Rich U.S. ores of copper, lead, manganese, and antimony gave no detectable signal, either because of faulty technique or because they are too weak. EPR signatures were obtained with most of the few ores tested. This encourages further study of EPR as an assay tool, and of the ENDOR (electron-nuclear double resonance) technique.

Subsequent to completion of the contract work, arrangements were made by Teledyne Geotech for 18 new ore samples to be tested for the ENDOR effect, by foremost U. S. experts in the technique. EPR signatures of at least 10 of the ores are also expected to be obtained. Those results are not yet available for inclusion in this report, so will be published elsewhere.

5. SYSTEM MODEL EXPERIMENTS

Shortly after discovery of the paper by Béné, we set set to work on an attempt to duplicate his experiments, with the aim of then extending them to external samples and to nuclei other than hydrogen. No experimental details or circuit diagrams were included in the papers by Béné's group. Nevertheless, their methods appeared to be just what we need for borehole assay logging.

In order to explore and become familiar with the practical advantages and limitations of Béné's method, a set of three orthogonal coils was wound on a piece of 1-1/4 inch PVC pipe as was shown in figure 15. Its parameters are given in figure 15. A 100 ml sample chamber with filler tubes was provided.

With the sample chamber filled with distilled water and the axis of coil A perpendicular to the earth's field (as determined with the gaussmeter), attempts were made to see the expected 1750 Hz decaying oscillation signal of the protons in coils B and C, without success. The oscilloscope amplifier was then supplemented with two low-noise preamplifiers and an adjustable bandpass filter to remove ambient electromagnetic noise (from fluorescent lights, radio transmitters, etc.). This too failed. (For one thing, the switching transient caused the filter to ring.) The magnetic gradient in the building from steel girders and furniture was measured and found unacceptable, so the experiment was moved outdoors, away from all iron, still without success.

In our second attempt to develop the electronics techniques needed to apply Prof. Béné's weak-field NMR methods to borehole logging, we planned to perform the following steps:

(1) Obtain a conventional proton-precession signal, using the earth's field and a strong, inhomogeneous prepolarizing field. Measure feasible signal/noise ratio.

(2) Repeat (1) with the proton sample outside of the prepolarizing and sensing coil. Measure relative signal strengths with internal/external samples.

(3) Repeat (1) using a strong, reversing secondary field (perhaps ac) instead of the earth's field. Determine signal enhancement obtained. Repeat with external proton sample.

(4) Using arrangement (3), substitute fluorite or phosphate ore for the proton-containing liquid, and attempt to measure its NMR signal. Repeat with external sample.

It can be seen that each step in the sequence requires that success be attained in the preceding steps. The lack of a visible proton signal from the coil system depicted in figure 15 was attributed to one or more of the

following causes:

(a) Excessive gradients in the earth's field indoors, because of steel in the building and furniture, which would spread the resonances of different parts of the sample to different frequencies.

(b) Too short a decay time T_1, from sample impurities or wrong sample substance.

(c) Too small a sample (for initial tests).

(d) Lack of hum-bucking coil design.

(e) Excessive ac fields in the environment, from power circuits and a powerful broadcast station only two miles away. (Lack of shielding?)

(f) Non-optimum bandpass filter characteristics and input amplifier noise figure.

(g) Insufficient polarizing field strength H_o.

(h) Scrambling of the proton precession orbits by a too-slow turn-off of the prepolarizing field Ho, and field oscillations below 1 gauss, where the vector sum of the earth's field and H_o is rapidly changing directions.

To eliminate (a) and (e), most experiments were performed outdoors as weather permitted, either in an empty lot near Geotech, or at a remote park 10 miles from the radio broadcast station.

To eliminate (c) and (d), and to prepare for the subsequent steps in our planned testing program, a new set of coils was designed and built, of the largest practicable size, as shown in figure 29. A plastic-pipe "borehole" and outer housing to contain the external samples were also prepared. The inner, big solenoid coil is wound in sections, with layers separated by 1/32" fiberglass strips, for maximum "Q". It consists of three sections, two hum-bucking end sections of 500 turns each, and a center section of 1000 turns which alone surrounds the internal 2.5 liter sample chamber. The two pairs of transverse coils have 282 turns of #18 wire and 1000 turns of #28 wire, respectively, to provide for a wide choice of inductances, pickup sensitivities, and current-carrying capacities.

In dealing with (b), we obtained distilled water with some difficulty; de-ionized water has largely displaced it commercially, but there are no published figures on T_1 for de-ionized water; its exact purity is uncertain. From reading and conversations with the makers of magnetometers, we learned that dissolved oxygen should be removed. This we did by bubbling helium through it overnight. We note that petroleum distillate or white gasoline is used in magnetometers, but this is evidently to prevent freezing.

To cope with (f), (g), and (h), a new filtered amplifier and switching circuit were breadboarded. The final schematic is shown in figure 16. Polarizing current of up to 4 amperes (giving an internal coil field of 92 gauss) is switched on and off the center 1000-turn portion of the large

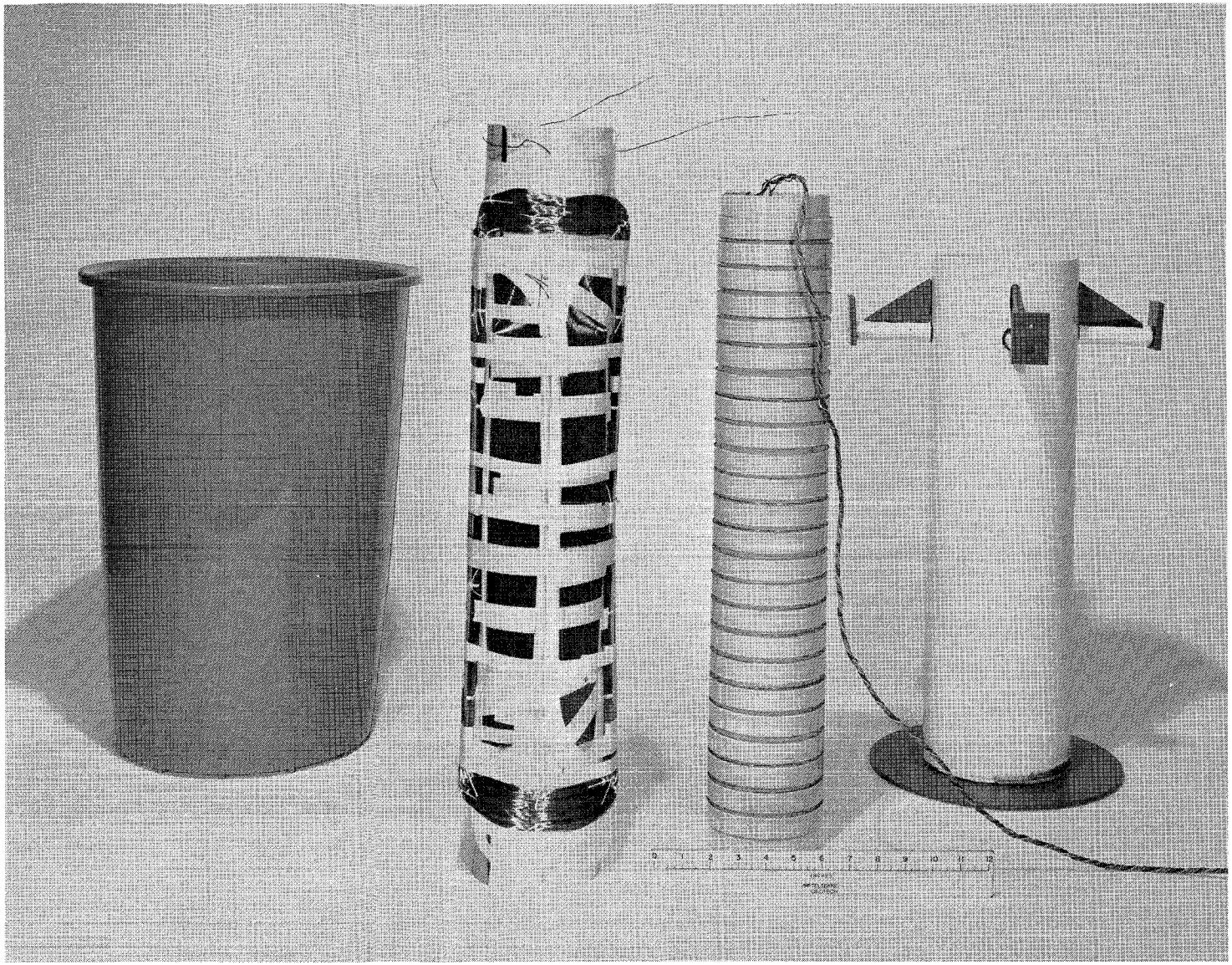


Figure 29. Large test model 1 to r: outer plastic container, transverse coils (taped but not wrapped), axial coil, plastic "well-bore"

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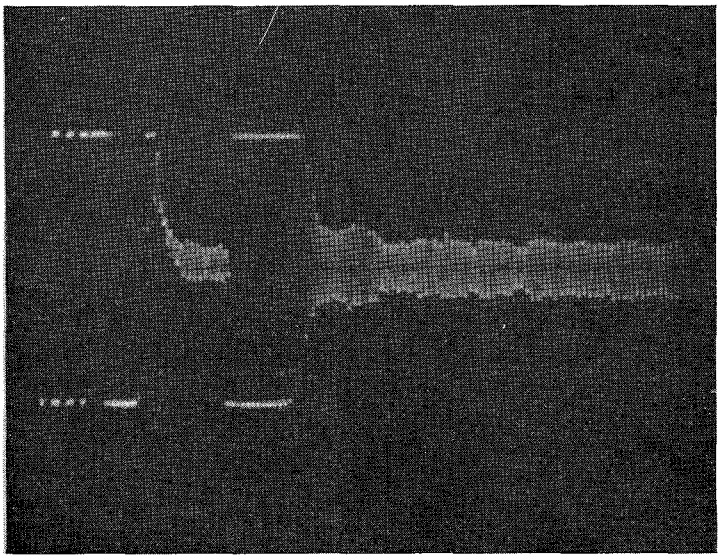
inner coil by the two power-Darlington devices (Delco DTS-4075) in series, controlled by a square-wave generator with a 1-second or 5-second period. These devices are capable of switching 1200 volts at 20 amperes in one microsecond.

As explained in section 3.3, the two Varo type 7704 avalanche diodes allow the induced spike voltage E to rise to 1100 volts, then hold it there while conducting the available current across this potential difference. Thus, they protect the DTS-40R5's from breakdown but dissipate the energy faster than any exponential process could do. With a 24 volt supply battery and 1/2 ampere of center-coil current, the current falls linearly with time to zero in only 30 microseconds. The slight overshoot and ringing can then readily be suppressed by the critical-damping resistor of 6200 ohms. The field passes through the critical values below 1 gauss (the last 8% of the current waveform) in a smooth, linear, nearly ideal manner.

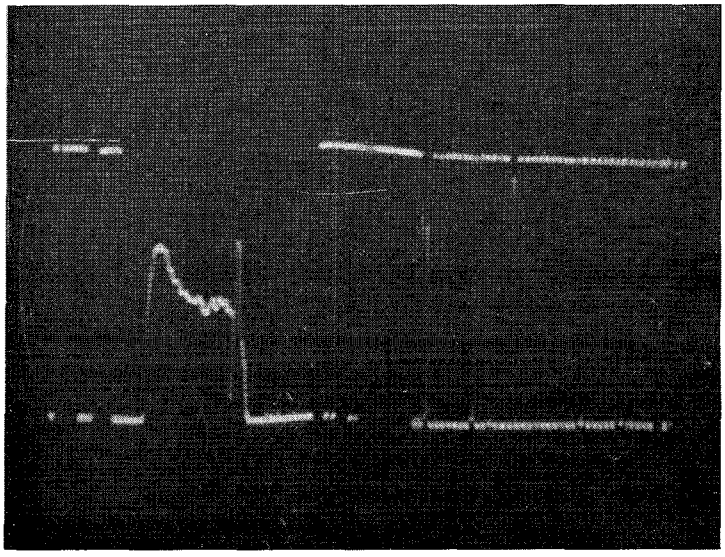
A few milliseconds after current cessation, the DPDT relay opens, disconnecting the charging circuit, and connecting the center coil section in series-bucking with the end coils and to the input amplifier. A type 739 op-amp is used for a good input noise figure. Measurements show that the amplifier produces between 0.3 and 0.6 microvolt (peak-to-peak) of semiconductor noise equivalent at the input. For its 3-dB filter bandwidth of 72 Hz centered at 2225 Hz, this is very good. The calculated thermal noise alone is 0.26 microvolt p-p for the estimated 7000 ohm input impedance of the big coil tuned with a shunt capacitor; measured noise for this coil, tuned and heavily shielded, was 0.8 microvolt p-p. This should be satisfactory since proton signals of tens or hundreds of microvolts are said to be achieved in magnetometers. The stable amplifier voltage gain of 700,000 (117 dB) is ample to drive a portable oscilloscope.

Initial field tests of the big solenoid coil of the logger model, with the breadboard circuit of figure 16 and with the internal tank filled with de-aerated distilled water, showed none of the expected proton signal with a long decay time of a second or so. Emphasis was therefore shifted to the study of the technology employed in commercial magnetometers.

Two GeoMetrics type G-816 portable proton-precession magnetometers were borrowed from friends in local oil companies. The manuals and a patent concerning them were studied, the analog portions of the circuits were traced (no schematics were obtainable) and the sensor coils were X-rayed to verify the hum-bucking arrangement. With these instruments, the magnetic field was explored in and around Geotech. Excessive gradients and/or extraneous ac fields were indicated by non-repeating readings. An acceptable test site 100 feet from Geotech buildings was found, providing the sensor coil was kept more than 10 inches above the soil. At this location, with a magnetometer giving a repeatable and correct reading of 52,550 +1 gammas, its amplifier output was as shown in figure 30 a, an oscilloscope photograph. The left, early part of the sweep is apparently dominated by switching transients. The frequency measurement was assumed to be completed during the 5-millisecond, squared (saturated) block just to the left of center, because the signal then decays rapidly below the level of what was believed to be steady noise to the right. This meant that the effective decay time constant for the white gasoline proton sample of this type of magnetometer would be only of



(a) With magnetometer, correct field reading, 50 msec sweep length



(b) With large coil and breadboard electronics. 200 ms sweep, 0.2 V/cm

Figure 30. Amplifier output waveforms, outdoor test area

the order of 3 milliseconds, which was very surprising; published values approach 1 second. Counting of the cycles per second in both the signal and noise portions of figure 30a gave about 2200 Hz; only the digital circuitry is capable of measuring the frequency with 5-figure accuracy, by timing the zero-crossings. The noise is confined to around 2200 Hz by the circuit filtering, but is no doubt frequency-modulated at random.

Figure 30b shows one result of many attempts to use our big coil, properly tuned with a shunt capacitor, as the sensor. The noise from this coil is much greater. It was not possible to test the functioning of our big sensor coil with the magnetometer electronics. An appropriate tuning capacitor, chosen by oscillator measurements, was placed in shunt in each test. Switching transients from the relay contacts occupy much of the first 40 milliseconds in figure 30b. Our narrow-band filter Q of 31 implies a ringdown time-constant of $Q/\Pi f_o$=4.4 milliseconds. The actual time constant measured is about 5 milliseconds. The inference was that no proton signal was seen with either coil.

Figure 30b also shows the input noise displayed by the breadboard electronics. This unusual noise pattern resembles that often picked up by circuits at Geotech from the nearby a-m broadcast station, except that it showed no regularities from musical tones, and did not correlate with the sound from a radio tuned to the station. It persisted when the equipment was moved to a distant park, when it was all heavily shielded and grounded, and regardless of which pickup coil was used, or even whether a resistor was substituted. It was certainly a feature of the narrow-band filter, since it became more like the broad-band noise of figure 30a when the filter was replaced with a resistor.

These early experiments illustrate the truism that in R and D, most attempts to do something new will fail. A certain level of experience must be attained through practice to succeed in any non-trivial technical effort. It simply takes time.

In accordance with consultant recommendations (Dr. Delmar O. Seevers, of Chevron), we performed further magnetometer surveys of several open areas on Geotech property near the main plant. The most acceptable working area found was in a small, grassy park shaded by mulberry trees and equipped with reinforced-concrete tables and seats. (The shade is essential for outdoor summer work in Texas.) Unfortunately, railroad tracks run within 150 feet to the east and northwest of this site, and several automobiles are normally parked 100 feet south of it. Nevertheless, a test area 6 ft x 8 ft x 8 ft high was found wherein the magnetic field was constant within ±100 gammas, with gradients near the center less than 7 gammas/foot.

A new series of experiments was begun with the magnetometer sensing head supported on its aluminum pole 6 ft above the soil, the magnetometer electronics 4 ft below it on a cardboard box, connected by coaxial cables to an oscilloscope and camera on the nearest concrete table 30 ft away. A series of tests was made wherein the bandpass-filtered (but mostly unclipped) signal from the first signal amplifier was monitored. A correct and constant magnetometer reading of about 52,150 gammas (repeating to within ±1 gamma) was used as the criterion that the proton signal was present. By destroying

the proton signal with a small magnet placed on the coil, we were finally able to identify the constant-amplitude but noisy "tail" shown in figure 30a as the proton signal; the larger events are mere switching transients.

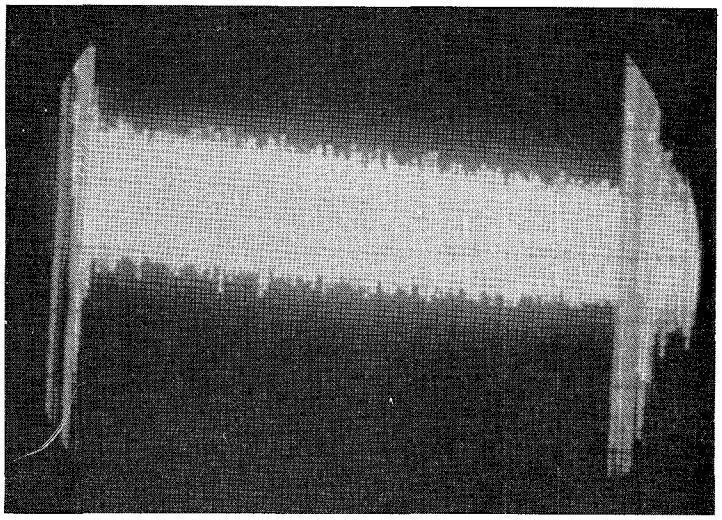
Figure 31 shows this "tail" displayed in its entirety, with the switching transients at the beginning and end of the magnetometer reading interval. The effect of nearby magnetic material in shortening the effective signal decay time can be clearly seen in figure 31(c). An even stronger magnetic gradient has destroyed the signal in figure 31(b), and the "field reading" now is merely noise, peaked near the center-frequency of the band-pass filter. The signal-decay time T_1 estimated for protons in white gasoline was estimated from figure 31(a) to be of the order of 2.5 seconds, in reasonable agreement with published values. The signal/noise voltage ratio, from a comparison of figures 31(a) and 31(b), was about 3. Thus, step (1) of the test procedure outlined above was successfully completed.

To proceed with step (2), two coils were prepared, which physically resembled the coil in the magnetometer sensing head and had the same inductance to permit proper tuning of the input circuit, which we could immerse in various liquids, place samples inside or outside of, etc. Each coil consisted of two identical, rectangular solenoids, of 2 in. x 3 in. x 3 in. long outside dimensions, fastened together side-by-side in a hum-bucking arrangement. The first coil was wound with 42/#40 single-nylon litz wire about 0.7 mm in diameter, and was dipped in RTV silicone rubber to exclude liquids from the wires. The second was wound with #21 solid, formvar wire and was impregnated with a clear polyester resin. (Thermalese-insulated solid wire had been tried, but shorted turns were found in the finished coils by means of Q-measurements). Each layer of wire in each coil was separated from the next by a thin polyester film to reduce the internal capacitance and thus increase the "Q".

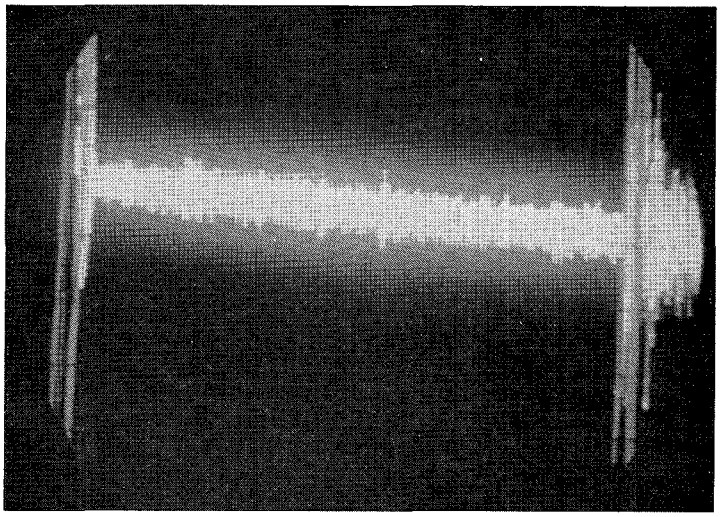
The first test coil gave good results with both distilled water and petroleum distillate samples. The hydrocarbon gave a slightly stronger signal, but not enough better to justify the greater difficulty of handling; it softened the silicone rubber on the coil, the vinyl bags used to contain it, and the adhesive tapes holding the parts together. We also found that ordinary tap water is nearly as good as distilled even with some impurity, so used tap water samples in all subsequent experiments.

Early attempts to compare the signal strength obtained when the coil is immersed (suspended and surrounded by 1 inch or more of liquid), with that with small bags of liquid inside the coils, and with the interiors filled with silicone-coated rubber sponges when the coil was immersed indicated that a reduced, but appreciable, signal can be obtained from the liquid on the outside of the coil.

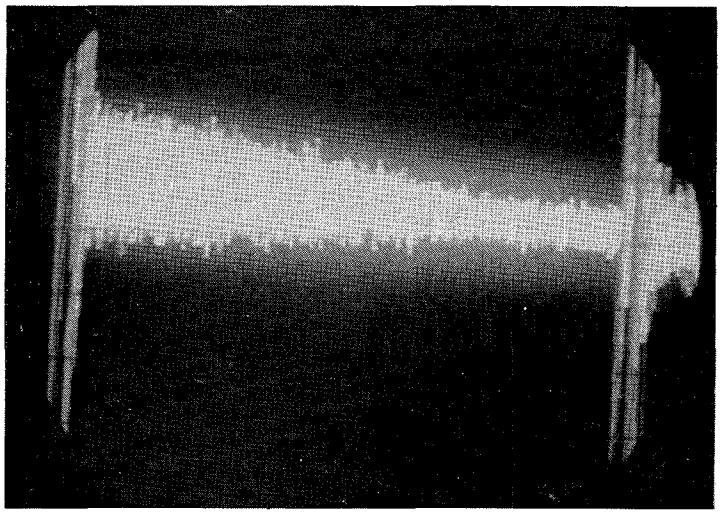
The second coil had a resistance of only 12 ohms (compared to 15 ohms for the magnetometer sensing head and 28 ohms for the litz coil). It carried correspondingly more prepolarizing current and gave a somewhat larger signal with tap water. A repeat of the external/internal experiment, using sealed, dry fiberglass boxes to fill the coil interiors, with the 1 mm gaps between box and coil sealed with tape, gave the result shown in figure 32.



(a) Sample and coil elevated 5 ft, in max, gradient of 8 gamma/ft.
Reading = 52,150 γ

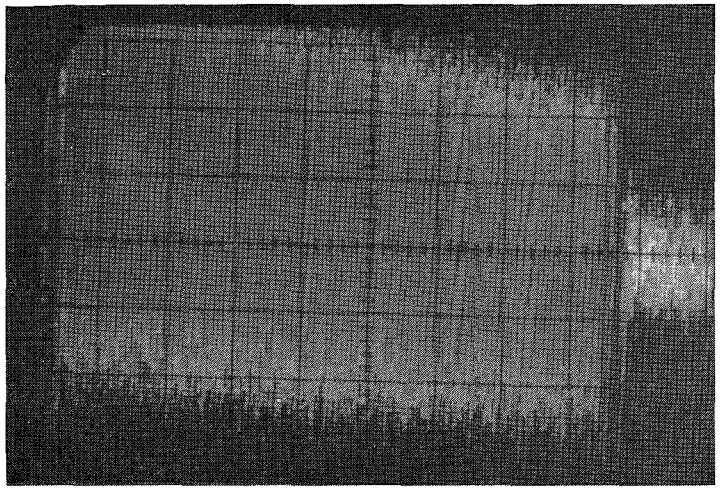


(b) Same as (a), with 1 lb iron hammer 2 in. away (signal spoiled).
Reading = 50,439 γ

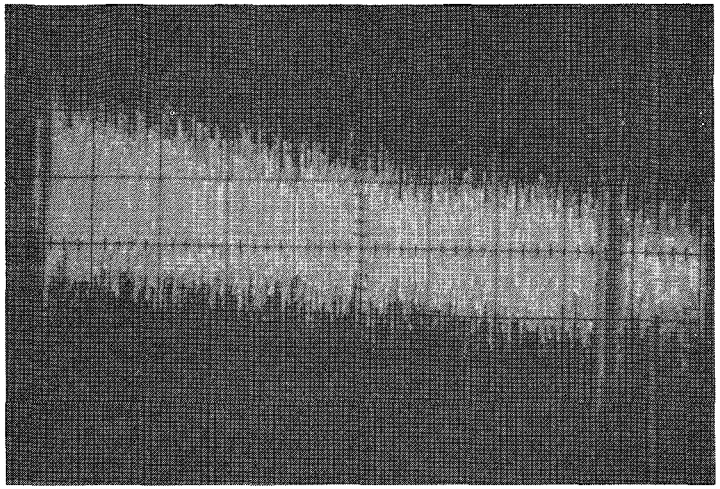


(c) Same as (a), with 1 lb hammer 10 in. away (proton precession decay time reduced to 0.3 second).
Reading = 51,868 γ

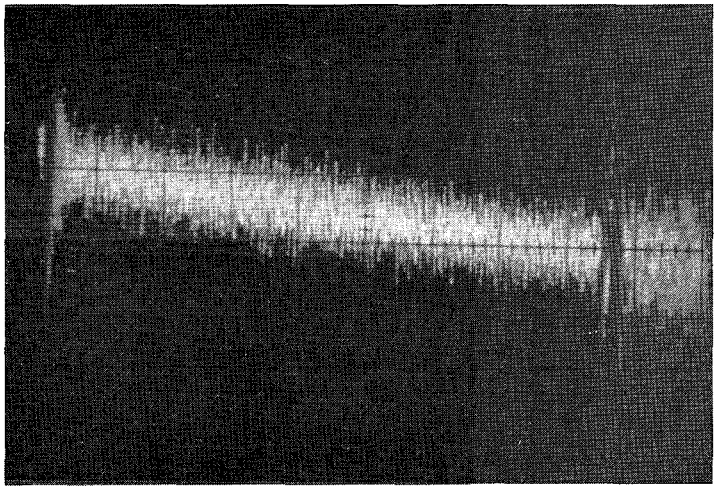
Figure 31. Magnetometer amplifier output.
Scales: 50 ms/div, horiz
20 mV/div, vert



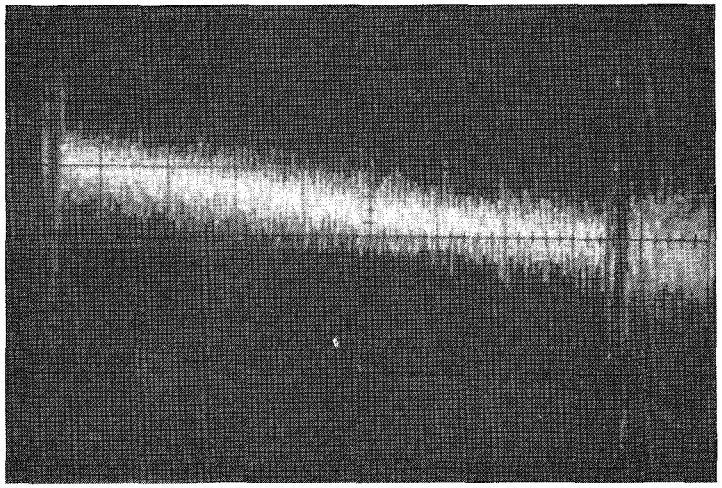
(a) Coils immersed



(b) Coils immersed, cores plugged



(c) Coils immersed, cores plugged, core gaps sealed



(d) Coils in free air

Figure 32. Proton signals, inside vs outside water samples (repeat). 0.01 V/div. (V), 0.05 s/div. (H)

With the cores plugged by the boxes (figure 32b), there is reduced signal strength. Nearly all of what remains is removed when the gaps are sealed (figure 32c). The difference between the remaining signal and the residual noise (figure 32d) is only about 10%, and cannot be measured accurately. It is clear that the "signal for an external sample" obtained at first must have arisen mostly from traces of liquid inside the coil and near its ends, when these were not thoroughly separated from the surrounding bath. We have observed (with a gaussmeter) that the prepolarizing field intensity generated outside of a solenoid is only of the order of 1% of that generated inside (see figure 15) while the "outside" field of a "transverse" coil is more like 10% of the "inside" field.

It is clear that "transverse" rectangular-loop coils should be used for all logging simulation tests in future. Although step "2" of our proposed procedure has now been carefully completed, it should obviously be repeated with a "transverse" coil to give results applicable to logging.

Subsequent to completion of the contract, system experiments were continued at Teledyne Geotech expense, with the aim of demonstrating one of the Béné techniques, if possible.

Because of its expected simplicity, the technique illustrated in figure 3 was chosen. The coil system shown in figure 15 was used, after modification. Coil A was used to pre-polarize the protons in the internal sample of water for 4 seconds at a field strength H_o of 96 gauss. Current was then rapidly switched from coil A to coil B, to produce a precession field H_1 of 12 gauss at right-angles to H_o. Upon establishment of this field, coil B was disconnected from coil A and connected to a resonating capacitor for a time interval of 225 microseconds. Switching was done entirely with high-voltage, solid-state devices.

Figure 33 shows the current (hence field) in coil B vs time. Although the initial part of the waveform is still contaminated with various transients, it can be seen that field H_1 begins at a maximum point in its cycle, at the moment that orthogonal field H_o collapses, and that it reverses twice at about 5 kHz, as required by the Béné method of figure 3.

Attempts were made to detect the expected proton pulse-echo signals in coil C (figure 15) at the times when H_1 was at its second and third peaks (arrows in figure 33). These signals should appear as short bursts of 51 kHz oscillation at those times. We have not yet succeeded at this writing, because of problems with the initial transients. These experiments may be reported in greater detail elsewhere.

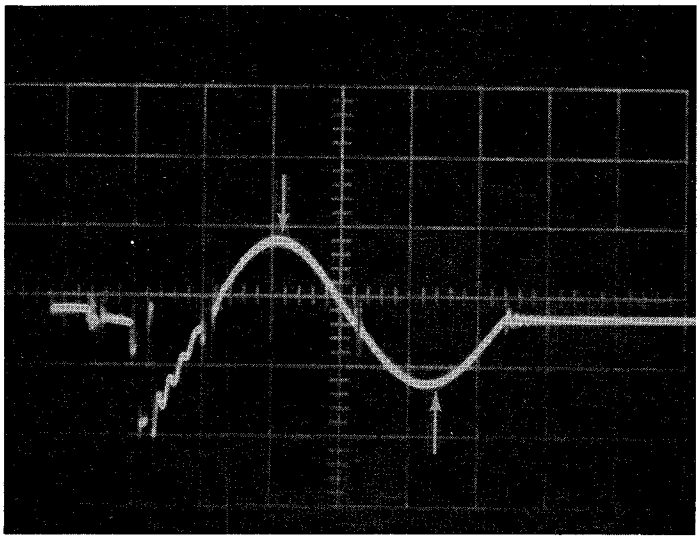


Figure 33. Current (field H_1) waveform in Béné system experiment. Scales: 50 microsec/div. horizontal, 12 gauss (1 amp)/ div. vertical.

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Herein are listed a number of important publications pertinent to this program, which are not mentioned or not given in full in the text of the report. They are grouped by subject, then by element. This list is representative of the literature found, but is not exhaustive.

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