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DEVELOPMENT OF ADVANCED MAGNETIC RESONANCE SENSOR FOR INDUSTRIAL APPLICATIONS

Final Report

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PREPARED FOR THE UNITED STATES
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Under Cooperative Agreement
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DISCLAIMER

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EXECUTIVE SUMMARY

Southwest Research Institute (SwRI) and various subcontractors, in a cooperative agreement with the DOE, have developed and tested an advanced magnetic resonance (MR) sensor for several industrial applications and made various market surveys. The original goal of the program was to develop an advanced moisture sensor to allow more precise and rapid control of drying processes so that energy and/or product would not be wasted. Over the course of the program, it was shown that energy savings were achievable but in many processes the return in investment did not justify the cost of a magnetic resonance sensor. However, in many processes, particularly chemical, petrochemical, paper and others, the return in investment can be very high as to easily justify the cost of a magnetic resonance sensor. In these industries, substantial improvements in product yield, quality, and efficiency in production can cause substantial energy savings and reductions in product wastage with substantial environmental effects.

The initial applications selected for this program included measurement of corn gluten at three different points and corn germ at one point in an American Maize corn processing plant. The development of the system and these earlier applications were described in detail in DOE publications DOE/ID/12726-1, November 1989; DOE/ID/12726-2, April 1991; and DOE/ID/12726-3, August 1994).

During the initial phases (I and II) of this program, SwRI developed a prototype advanced moisture sensor utilizing NMR technology capable of accurately and reliably measuring moisture in industrial applications and tested the sensor in the laboratory under conditions simulating on-line products in the corn wet milling industry. The objective of Phase III was to test the prototype sensor in the plant environment to determine robustness, reliability and long term stability. Meeting these objectives would permit extended field testing to improve the statistical database used to calibrate the sensor and subject the sensor to true variations in operating conditions encountered in the process rather than those which could only be simulated in the laboratory.

In Phase III of the program, successful tests were conducted the four different locations in the American Maize corn wet milling plant in Dimmitt, Texas. A fifth test was conducted, after returning the system to the laboratory, on dried milk samples from DCCA (Dairymen's Cooperative Creamery Association) to show the system's diverse capabilities. Extended field testing successfully demonstrated robustness, reliability and stability in the plant environment. The NMR sensor's electronic hardware, in itself, did not once fail or malfunction during the field test period. Software modifications were made to accommodate unusual signal conditions encountered during process startup and shutdown.

Some mechanical problems were encountered with the sampling apparatus. In one case, product leaked and was trapped between the sampling piston and cylinder causing the need for a substantially increased force to move the piston up and down. The increased force caused one of the sampling components to fail. The component was upgraded during the field test. This problem would not have occurred if the sampling drawer, which provided a means to remove the actual samples subjected to NMR measurement for standard laboratory analysis, had not been used. The transitions caused by the drawer allowed leakage that would have occurred in a smooth tube (cylinder).

A second problem involved material handling at one of the test sites (rotary vacuum filter output.) Wet gluten (~55-60% on a wet basis) stuck to and clogged the output chute of the sampling system. This prevented unattended operation at this site as the exit trough from the screw conveyor became plugged within 1-3 days if left unattended. It should be noted that American Maize does not try to handle this product in any conveyor. This product normally falls from the rotary vacuum filter output and is mixed with recirculated dry gluten (~12% moisture) in a long screw conveyor to achieve a moisture level (~48% moisture) which makes the material much easier to handle. These severe handling problems were not anticipated when this site was chosen. American Maize stated knowing the moisture at this point would be of interest, but the product was too difficult to handle.

The correlations between NMR data and laboratory gravimetric moisture measurements were quite good once problems with laboratory reference measurements were resolved. Some modifications were also made to the NMR magnet and sample coil to obtain a more rigid assembly which would not be affected by high levels of vibration encountered in the plant. Typical standard errors encountered in the corn gluten measurements were 0.3% moisture (the goal was 0.1-0.2%). Considering the accuracy limitations of the gravimetric methods and the high level of product handing and shipping delays to the point at which the gravimetric methods could be applied, the results were reasonable. The laboratory measurements of corn germ and dried milk product moisture showed good correlations to gravimetric methods for reasonable moisture ranges. However, the corn germ and milk product moisture ranges encountered in the process were very small. Standard deviations for corn germ was typically 0.4% and for a dried milk product was typically 0.1%. Reasonable correlations between NMR and gravimetric data can not be obtained for very low moisture ranges.

The system is capable of measuring moisture values over the range of one to over 60 percent moisture wet basis (almost twice the range requested in the original Program Research and Development Announcement). The results were very encouraging. Since this device was a prototype, flexibility was emphasized at the expense of potential production cost. With optimum specifications defined, production units can be designed and constructed with concomitant cost savings. To this end, additional work directed towards economic and technical feasibility of commercializing an advanced MR sensor was conducted. Borrowing from the historical information of the development of other on-line sensors (process GC, NDIR, NIR, Mass spec, capacitance, nuclear, microwave, etc.), the coordinators of the market survey predicted a relatively slow development of the market ($5-10M by the end of the decade). An extensive market survey report and bibliography were provided by the marketing consultants (PAI Partners and Townsend Agency) to DOE, QM, and SwRI.

A later application for which the system was applied to was the measurement of the rheological properties of black liquor used in paper mills. Within this recent work, a cost and preliminary performance analysis of rheological property measurement applications was performed. The results of these analyses were used as a basis for a market study. End users and equipment suppliers were contacted. Market size and price elasticity was determined, and competing technologies and any significant barriers to market penetration were identified.

To determine the suitability to this application, laboratory measurements on several representative samples of black liquor were made at temperatures from 25 to 130°C and pressures typically present on a black liquor sampling stream. Conventional relaxation, quantitative, and self-diffusion data was obtained. From this data, operational requirements for the previously developed MR system were determined.

Modifications were made to the system. Modifications included high temperature/pressure handling, flow stream heating for maintaining nominal product temperature, flow stream interface, and control and signal processing changes. A several month flow loop test at the University of Florida (UF) was carried out. The substantial data was collected, analyzed, interpreted and compared to standard data.

The data indicated that the MR relaxation parameters for a given black liquor correlate well with the viscosity of a given black liquor. Changes in the composition of the black liquor (e.g. the differences that exist between the Canadian Forest and Georgia Pacific black liquors) also effect the MR relaxation times irrespective of the viscosity. In other words, the MR viscometer can provide quantitative viscosity information if the nature of the black liquor is known, but the technique breaks down if there are large changes in the composition of the black liquor. The lack of correlation between the MR relaxation times and the viscosity does not imply a breakdown in the theory presented. The relaxation theory does not take into account changes in the composition of the materials being investigated, so one cannot expect that the relations will necessarily hold for black liquor samples taken from very different sources.

When we make the conclusion that the MR data does not correlate well with the viscosity when the black liquor composition is unknown, we are assuming that the HAAKE viscometer data obtained by UF is correct. If for some reason the conventional viscometer data is wrong, then we have no way to correlate the MR data with a known viscosity.

The MR viscometer data is somewhat effected by flow, but these flow effects may be avoided by changing the geometry of the transmit/receive rf coil system. If the transmit coil is larger than the detection coil, then flow will cause an apparent reduction in the MR relaxation times.

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1. BACKGROUND AND INTRODUCTION

In 1988, Southwest Research Institute (SwRI) entered into an cooperative agreement with the Department of Energy (DOE) to develop an advanced on-line moisture sensor for application to industrial drying processes. The primary goal of Cooperative Agreement # DE-FC36-88ID12726 has been to reduce energy consumption by increasing drying efficiency. The technology employed in development of the sensor is magnetic resonance (MR). Design objectives for the sensor included: real time on-line measurement over the range of 2 to 70% wt moisture (wb), reliable operation with sample temperatures to 350°F in harsh environments, and a design that would be economical to produce and maintain.

The Advanced Moisture Sensor Research and Development program, which began in April of 1988, was originally proposed with three phases (concept development and laboratory study, prototype fabrication and testing, and industrial testing and verification). These original three phases were successfully completed. The Technology Transfer (Task 5) portion of Phase 3 was extended to evaluate the economic and technical feasibility of commercializing the advanced moisture sensor prototype unit. This extension was partially completed as will be summarized in Section 4.6. An additional effort provided for additional investigations and analyses into reological applications of NMR. Within this additional effort, the following tasks were performed: cost and market analyses, laboratory measurements on black liquor products, modification of the previously developed NMR system to accommodate flowing black liquor product at process temperatures, flow loop tests at the University of Florida in Gainesville, and analysis of the collected laboratory and flow loop data and reporting of the findings. The overall program is described in the following paragraphs.

2. PHASE 1 - CONCEPT DEVELOPMENT AND LABORATORY STUDY

A Concept Development and Laboratory Study was conducted to determine the technical and economic feasibility of the proposed sensor. Meeting the objectives of this effort resulted in the development of a rugged low maintenance MR sensor as well as innovative measurement techniques widely applicable to process control in industrial plants. The phase included three tasks:

2.1 Task 1- Develop Sensor Concept & Investigate Feasibility

A literature search was performed to examine other techniques for monitoring moisture in drying processes. The search revealed 45 potentially useful papers of which 30 were relevant to the program. The conclusions of the literature survey were that magnetic resonance is an attractive sensing technique offering high accuracy, reliability, and flexibility without sensitivity to a number of extraneous parameters such as sample packing density and homogeneity.

Applicable processes representing major users of industrial drying energy including agricultural products, food processing, lumber and wood products, textiles, and paper were investigated. From these industries, corn wet milling, the largest single user of industrial drying energy, was selected as the most appropriate process. An American Maize corn wet milling plant in Dimmitt, Texas, agreed to participate in the program.

After significant investigation and experimental efforts, a development plan for the HTNMR probe was defined. It was determined that a piston sampling system, which was later patented, would optimize the probe configuration. A resonant frequency of 11.25 MHZ was selected to allow use of a relatively low cost permanent magnet.

2.2 Task 2 - Develop Sensor System

During this task, the sensor, sampler and environmental simulator were designed and fabricated. Additionally, a test plan and matrix for evaluation of the sensor was developed and approved. Costs were minimized by concentrating only on the probe (magnet, sensor coil, and tuning capacitor) design and utilizing laboratory electronics for testing. It was decided to postpone development of electronics for the probe until Phase 2 of the program. Following completion of designs, the probe and sampler were fabricated, debugged, and successfully performance tested. After minor modifications, the experimental tests, as defined in the approved test matrix, were conducted.

2.3 Task 3 - Verification of Technical & Economic Feasibility

The probe was experimentally tested by conducting measurements on samples from the matrix as described in the test plan. Results of testing showed that using FID data, moisture measurements were feasible to levels of 35% and by using CPMG data, accurate measurements could be made to levels of ~70%; by combination, it is technically feasible to make measurements in the range of 0 to 70%. Additionally, an offset preventing the curve from passing through the origin was attributed to oil content.

While costs of energy saved by using the sensor was determined to be small, it was demonstrated that deployment of the sensor was economically feasible. Accurate control of moisture content to prevent overdrying products sold by weight results in more product sold. In the corn wet milling operation, controlling moisture content to an allowable 12% would result in an additional $75,000 of product sold annually, more than offsetting the projected sensor cost.

3. PHASE 2 - PROTOTYPE FABRICATION AND TESTING

Prototype Sensor Fabrication and Testing encompassed design, construction, and laboratory testing of a complete MR system incorporating the sensor from Phase I. The design objectives were attained with the inclusion of several novel features resulting in a state-of-the-art system for field testing.

3.1 Task 1 - System Design and Fabrication

Figure 1 is a block diagram of the MR prototype system designed and fabricated during this task. An industrial computer (IBM AT compatible with passive backplane) was incorporated for system control and data analysis. Control information to define pulse sequences required for a particular experiment are transferred from the computer to the pulse programmer. Logic pulses from the pulse programmer are used to gate phased RF bursts in the Oscillator and RF Switch unit. The generated RF burst stream is coupled to the input of the RF pulse amplifier. The RF power amplifier output is coupled via the T/R network to the MR probe. Low level signals from the probe are coupled via the T/R network to the preamplifier and receiver; the output of which is digitized. The computer reads and analyzes the digital signals and calculates moisture content which is displayed on the front panel and converted to a 4-20 ma signal for use by other systems. Additionally, the computer monitors system status and controls the sampling mechanism.

The system, as described, was fabricated with the probe and sampling mechanism being installed in a separate package from the electronics. The electronics were housed in a NEMA 4X stainless steel enclosure intentionally oversized to provide access for adjustment and modification. Appropriate software for the computer was written and debugged on the operating system.

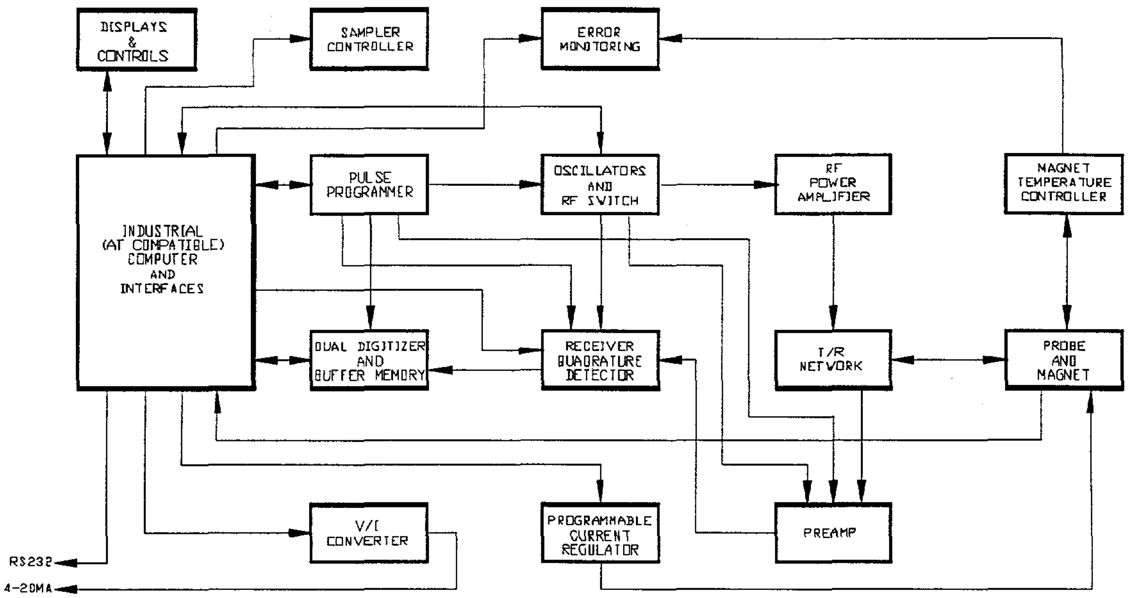

Figure 1. MR System Block Diagram

3.2 Task 2 - Lab Testing and Analysis

Extensive testing of the HTNMR system in the laboratory was conducted using the test plan and environmental simulator. Analysis of test data determined techniques to be used in field testing. The sensing technique was found to be applicable to moisture measurement over a range of 0 - 70% (wb) and also capable of simultaneously determining oil content of the product. The piston sampling system performed satisfactorily and the electronic system proved to be reliable and accurate.

4. PHASE 3 - INDUSTRIAL TESTING AND VERIFICATION

Industrial Testing and Verification, commenced in June of 1991. Successful tests have been conducted at four different locations in a corn wet milling plant. A fifth test was conducted after returning the system to the SwRI laboratory on dried milk products to confirm the system's diverse capabilities.

4.1 Task 1 - Dryer Output Test

The first field test was conducted on gluten at the flash dryer output which should output gluten with a nominal 12% (wb) moisture content. Because this was the first field test, several system problems were encountered and solved during installation and setup before meaningful results were obtained. Additionally, initial independent laboratory test results were deficient and a credible source had to be established before correlation with field data could be made. After the difficulties were alleviated, however, the test was completed successfully. Good correlation was demonstrated between MR measurements and laboratory analysis of samples. Standard deviation for moisture differences between field measurements and laboratory analysis was 0.37%, which was considered good, although short of the 0.2% goal.

4.2 Task 2 - Dryer Input Test

Gluten at the dryer input was monitored during the second field test. Moisture content was nominally 48% (wb). Minor mechanical modifications to the sensor were required, but following installation, successful testing commenced. Results were comparable to the first test; correlation between field measurements and laboratory analysis for moisture within 0.3% to 0.4%.

4.3 Task 3 - Rotary Vacuum Filter (RVF) Output

Following completion of testing at the gluten dryer input, the system was returned to SwRI for fitting and testing with a conveyor required for testing at the third site. High moisture content (~55% wb) and cohesiveness of the gluten at the RVF output caused unanticipated handling problems requiring additional mechanical modifications to the system before testing could begin. Once the handling problems were addressed, testing results comparable to those from the dryer input test were attained. It was not possible to conduct long term tests at this site due to blockages of the material after a period of a few days.

4.4 Task 8 - Germ Dryer Output

Before testing at the germ dryer output, a different conveyer was fabricated and installed; however, as in the other three tests, no changes were required to the sensor. Field testing was completed successfully at the fourth site. Laboratory analysis and data correlation yielded results not as good as had been obtained on the gluten. The dried germ typically has low moisture (2 to 4%) and high oil content (~50%). It was difficult to measure a low amount of moisture in a high level of oil.

4.5 Task 9 - Powdered Milk Products

Other agricultural food products, including onions, garlic, carrots, squash, and milk products were investigated and tested in the laboratory as candidates for a fifth test. Of these, milk products were most promising. Further testing on powdered milk were conducted at SwRI using the field system. Results were generally satisfactory.

4.6 Extended Task 5 - Economic and Technical Feasibility of Commercializing Advanced MR Sensor

SwRI developed a field-worthy engineering prototype with substantial capabilities that has been extensively tested for performance reliability and accuracy. The comprehensive experience of the SwRI team, gained from this program as well as many years involvement in the development of advanced industrial sensors, has resulted in the evolution of a MR system with outstanding features including:

- Applicability
  - Agricultural Products / Food Processing
  - Wood / Wood Products / Paper
  - Chemical/Petrochemical Processes
  - Textile
  - Coal
- Adaptability
  - Flowing products in pipes
  - Moving products on belts, conveyors, or chutes
  - Sheet products (paper)
  - Direct or via sampling mechanisms

- Measurability
  - Independent of distribution
  - Direct weight percent moisture
  - Quantitative by binding states

It was perceived that a substantial market existed for this system when further development into a cost effective production system was pursued. The DOE authorized SwRI to continue the cooperative agreement as a technology transfer to an appropriate commercial enterprise (industrial partner) for the purpose of industrial application of the sensor.

Quantum Magnetics of San Diego, California (QM) was selected and agreed to be the industrial partner with SwRI for this technology transfer. As such, Quantum was to be responsible for marketing, manufacturing, sales, and service of eventual products.

Although significant knowledge was gained from applying the advanced moisture sensor in a corn wet milling plant, effecting solutions to many technical problems, little factual data was gathered, or existed, regarding market potential for industrial magnetic resonance sensors. Addressing the market and determining probability of success were the objectives of this phase.

4.6.1 Preliminary Product Specification

The prototype MR advanced moisture sensor was developed to be extremely versatile and functionally adaptable with minimal consideration given to cost or manufacturability. A preliminary product specification was produced to document initial understanding of requirements for the production industrial MR. Particular emphasis was given to industrial user requirements including ease of integration and minimization of service and maintenance.

The following areas in the previously developed system were cited where improvements could be done:

- Durability and Leak Resistance of Sampler (potentially replace with a pneumatic/hydraulic approach)
- Homogeneity and Temperature Stability of the Magnet
- Include a Programmable Logic Controller PLC and Temperature Control at the Sensor location to minimize control wiring
- Better sense the product temperature
- Go to a more serviceable and more compact bus for the computer (i.e. STD bus)
- Upgrade the NMR Low-Level Electronics

  - Eliminate all relays (use wide band analog switches)
  - Use multilayer PC boards for straight line signal flow and combining digital inputs
  - Move Pulse Programmer and Digitizer to computer bus
  - Use multiple coax connectors and/or push on coax connectors where possible
  - Replace hybrid amps in RF stages with smaller, cheaper, and lower power alternatives
  - Add sealed plant-type PC Display and limited sealed keyboard to control unit

The preliminary product specification in its initial form was used to generate the specification sheets distributed for the market survey.

4.6.2 Preliminary Production Design/Cost Analysis

A preliminary design with sufficient detail to permit cost analysis was performed. The design embodied the approved product specification and had sufficient detail to allow determination of approximate cost to build as a function of configuration and quantity.

The magnet is currently the most expensive component in the MR sensor. Within the current design, a stable and homogeneous magnetic field is critical for accurate measurements. A review was conducted to determine actual requirements for the magnet and investigate alternatives to the current design that could result in a lower cost and more reliable magnet system.

The most critical component, from a reliability perspective, is the sampler used to convey product through the probe (magnet and sample coil). Because the sampler contains moving parts, it is a weak link; however, also extremely significant because sampling may provide a uniquely simple method of measurement that could standardize the magnet independent of application. The risks of using a sampling system versus the cost impact of variable size magnets were examined and evaluated.

A preliminary design was executed utilizing the product specification, existing design documentation, and results from the magnet requirements review task. Some electrical, mechanical, and system engineering were performed to provide the basis for determination of probable manufacturing costs.

4.6.3 Market Definition/Survey

Market research was performed by two outside firms (PAI Partners and Townsend Agency) specializing in industrial marketing. The research included four tasks: market research and definition, focus group studies, a questionnaire survey, and a report of findings.

Meetings attended included the International Food Technology (IFT) show and the Instrument Society of America (ISA) Conference in August and October 1994, respectively.

After a detailed survey of available market research literature, additional requirements were defined and the indicated market research conducted. The research results, among other things, predicted:

- Market size and most promising niches,
- Customer needed features and relative importance,
- Expected pricing and price elasticity of demand,
- Expected market growth, and
- Base for product specification and marketing plan.

To design the questionnaire for use in the field survey, results from the market research were analyzed and a sample frame developed. From the sample frame, a population was defined. The questionnaire was generated using the hypothesis developed.

The field survey was conducted using telephone interviews of a sample of the selected population. A mail survey was also conducted. There were a total of 85 respondents.

Results of the market research and field survey were detailed in an extensive report provided by PAI Partners and Townsend Agency. A summary of this report is included in Appendix A.

The data (product) sheet, survey questionnaire, and cover letter mailed to representatives of various selected industries are shown.

PAI Partners received mail survey responses and conducted telephone and personal interviews concerning the advanced moisture detection system. A number of the telephone interviews duplicate the mail responses, but the total number of individuals were 85.

The industries represented by the 85 individuals are as follows:

Petroleum	7
Petrochemical	7
Agricultural Chemicals	3
Other Chemical	11
Pharmaceutical	10
Food Processing	21
Rubber and Plastics	3
Metals	2
Textiles	2
Animal Feed	3
Pulp and Paper	1
Other	15

Food processing firms included General Foods, Kraft, Nabisco, Hershey, McCormick, American Basic Foods and Universal Foods. Chemical and petrochemical forms included Amoco, Dow, Dow Corning, Dupont, Monsanto, and Union Carbide. Pharmaceutical firms included Burroughs-Wellcome, Lilly, and Merck. Pulp/paper and other firms included Georgia Pacific and UOP.

The two major respondent groups are interested in different applications. The Food Processing group are primarily interested in moisture determinations in the percentage range and determinations of fat and oil. The Petrochemicals group are interested in trace moisture and a range of other assays.

Recommendations resulting from the market survey were:

1) Form application partnerships in the following areas
   - Polyolefin
   - Pharmaceuticals
   - Processed Foods
2) - Form an advisory panel

Summary items resulting from the market survey included:

1) Instrument manufacturer must become knowledgeable about the processes of potential customers
2) The supplier must have full sample data prior to quotation
3) Cooperative arrangements with customers benefit both parties
4) The supplier must take application responsibility
5) The instrument design should be standardized to some degree but also simple to alter
6) Process customers, unlike lab customers, seek a solution to a specific application need

Borrowing from the historical information of on the development of other on-line sensors (process GC, NDIR, NIR, Mass spec, capacitance, nuclear, microwave, etc.), the coordinators of the market survey predicted a relatively slow development of the market ($5-10M by the end of the decade). An extensive market survey report and bibliography were provided by the marketing consultants (PAI Partners and Townsend Agency) to DOE, QM, and SwRI. A condensed version of the report is included in Appendix A.

4.6.4 Analysis / Go - No Go

Following submission of the marketing report, DOE, SwRI, and Quantum analyzed and evaluated the information. There was a consensus that a limited market existed for an advanced moisture sensor. A slow growing market was predicted and considerable inroads by existing MR sensor companies caused a redirection of the program in line with the new proposed effort into rheological applications.

5. RHEOLOGICAL APPLICATIONS

The work for rheological applications was accomplished in the following five (5) tasks.

5.1 Task 1 - Cost and Market Analyses

A cost and preliminary performance analysis of rheological property measurement applications utilizing NMR technology was performed. Applications included black liquor and other liquor measurements, polymers, chemical, petrochemical and petroleum products. The results of these analyses were used as a basis for a market study. End users and equipment suppliers were contacted. Market size and price elasticity was determined. Competing technologies and any significant barriers to market penetration were identified. A document prepared by Dr. Geoff Barrall of QM including a concise explanation of NMR theory and relationships to viscosity and brief descriptions of competing viscometers is included in Appendix B.

QM who is primarily responsible for this task has subcontracted part of the Market Analyses task to The Townsend Agency (TTA), San Diego, Ca. TTA began by developing a schedule for the market study which has been followed by both QM and TTA. After developing the market study time line, TTA researched pulp and paper industry trade shows to determine which should be attended as part of the market study. QM provided TTA with a summary of the technical information acquired to date on the project. Both QM and TTA used this information to develop a list of interview questions to be asked of potential competitors (rheometer and viscometer companies) and U. S. Department of Energy university and industry representatives. QM performed an extensive literature and patent search which is currently being reviewed for relevant journal articles, government reports and patents.

Using the results of the scheduled interviews, a end-user survey to distribute among industry representatives was compiled. Distribution included mail surveys, phone surveys and personal interviews at the TAPPI Engineering Conference (September 16-19, 1996, Chicago, IL). Armando De Los Santos of SwRI and Geoff Barrall of Quantum Magnetics attended a black liquor review meeting at the University of Florida (UF) on 15 August 1996. Some communications with representatives of paper mills were conducted. While the NMR data correlations to reference viscosity measurements were consistent for types of black liquor, correlations to a variety of different black liquor types were not as good as desired. Additional data was provided at the time of the meeting for additional correlation studies. However, NMR has the capability to measure more aspects of black liquor properties such as solids content, sodium content and potentially carbon content. This was of interest to the paper mill representatives.

Geoff Barrall of QM and Jackie Townsend of The Townsend Agency (TTA) attended the TAPPI Engineering Conference (September 16-19, 1996, Chicago, IL) where more end-user industry representatives were interviewed. A questionnaire was distributed and collected during the conference. Some additional personal interviews were performed. The market study report is included in Appendix C.

5.2 Task 2 - Laboratory Measurements

During the second task, laboratory measurements of black liquor samples were made. Measurements were made on 12 representative samples at temperatures from 25 to 130 C at typical pressures present on the sampling stream. Conventional relaxation, quantitative, and self-diffusion data was obtained. From this data, the operational requirements modifications to the existing DOE system were determined. Constraints were reasonable modifications to the existing system which will be addressed in the third task.

Dr. Oscar Crisalle and graduate student, Mr. Tony Dutka, provided 12 black liquor samples. The solids content of the samples ranged from 28.34% to 82.06%. Relaxation data, T_1 and T_2, was taken at room temperature, 100°C, 120°C, and 140°C. Some of this data is summarized in Tables 1 and 2. The T_1 data shows a consistent variation with solids content within temperature ranges with the exception of sample 6 which shows characteristics similar to samples 9 and 10. From these initial results, we expect the T_1 measurement to provide the best correlation to the solids content/viscosity of the black liquor. The system was programmed to also make the T_2 and signal magnitude measurements during the field tests. Due to the difficulty in achieving uniform sample temperature during laboratory tests, some inconsistencies in this data is expected.

The correlations between solids content, viscosity and the NMR relaxation times were good with the exception of samples 3 and 6. After discussions with the UF personnel, it was clarified that these two samples were of a different type of black liquor. From the limited data taken in the lab, a relationship between the NMR parameters and provided black liquor data was determined. From this initial data, the T_1 measurement provided the best correlation to the solids content/viscosity of the black liquor. The preliminary relationship between T_1 and viscosity is shown in Figure 2. Some extrapolation was necessary to generate this curve. The system was also programmed to make the T_2 and signal magnitude measurements during the field tests.

TABLE 1. SPIN LATTICE (T_1) RELAXATION DATA

Sample No.	Solids (%)	T_1 (msec) Rm. Temp.	100°C	120°C	140°C
1	28.34	169.31	567.8	775.5	838.0
2	35.78	97.44	277.1	549.2	631.1
3	42.20	48.64	273.3	272.3	413.3
4	43.64	51.65	282.5	351.3	403.8
5	50.59	36.18	198.2	250.7	327.1
6	55.00	18.86	68.0	94.6	189.2
7	57.24	21.00	122.6	166.8	235.0
8	59.53	20.67	98.5	134.2	175.0
9	63.80	17.06	90.6	124.1	178.4
10	67.88	15.45	68.2	93.8	130.4
11	75.94	*	47.4	60.5	85.1
12	82.06	12.78	45.5	67.6	99.3

* Not Measured
Samples from Georgia Pacific, Chesapeake Paper ABAFX031,32

TABLE 2. SPIN-SPIN (T_2) RELAXATION DATA

Sample	Solids	T_2	T_{22} 100°C		T_{21} 100°C		T_{22} 120°C		T_{21} 120°C		T_{22} 140°C		T_{21} 140°C	
No.	(%)	Rm Temp		%A		%A		%A		%A		%A		%A
1	28.34	104.62	637.8	74.3	125.7	25.7	724.1	81.0	115.8	19.0	772.6	91.2	57.9	8.8
2	35.78	67.76	288.2	69.7	64.5	30.3	464.8	86.5	64.3	13.5	512.1	84.5	54.7	15.5
3	42.20	30.74	320.9	57.7	79.9	42.3	264.8	54.4	69.9	45.6	296.4	65.4	70.0	34.6
4	43.64	33.31	368.6	66.1	79.3	33.9	394.5	78.4	70.3	21.6	418.6	82.6	63.6	17.4
5	50.59	21.22	170.9	79.9	37.9	20.1	218.3	81.6	30.4	18.4	262.7	84.6	31.9	15.4
6	55.00	8.65	190.3	20.2	30.0	79.8	162.4	31.7	34.6	68.3	169.9	64.8	31.6	35.2
7	57.24	10.43	114.8	71.8	34.5	28.2	140.8	81.9	33.6	18.1	202.1	79.5	33.9	20.5
8	59.53	8.83	128.8	43.3	33.3	56.7	130.9	72.3	37.9	27.7	158.1	76.1	31.3	23.9
9	63.80	6.06	118.2	34.2	33.2	65.8	124.5	67.8	32.3	32.2	156.9	72.4	30.3	27.6
10	67.88	3.93	115.9	19.3	27.5	80.7	92.6	54.5	30.2	45.5	122.8	67.3	28.2	32.7
11	75.94	*	245.3	9.2	20.6	91.8	81.1	24.5	23.8	75.5	113.8	43.5	32.1	56.5
12	82.06	1.14	195.5	4.9	17.2	95.1	126.2	15.6	25.9	84.4	103.6	42.8	30.9	57.2

*Not Measured

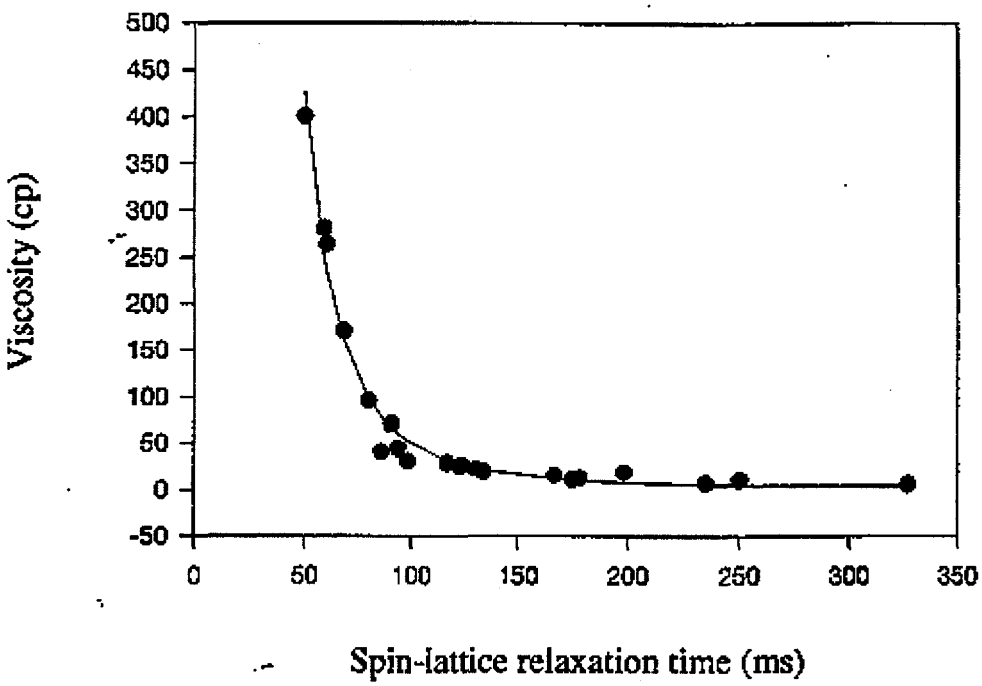

Figure 2. Viscosity versus T_1 over a wide temperature range (90° - 140°C)

QM also analyzed the NMR laboratory results provided by SwRI. These results included data from both the T_1 and T_2 relaxation time experiments conducted over a wide range of temperatures on black liquor samples of varying solids content. QM analyzed the data to determine the correlation between the NMR results and the black liquor solids content. These preliminary results indicate that there is a strong correlation between the black liquor solids content and the NMR relaxation times and signal amplitudes. QM also corresponded with UF to gain more detailed information on the test samples provided to SwRI. UF was not able to provide the information necessary to correlate the NMR data to the black liquor viscosities over the range of temperature in the experiments, so QM will not attempt to correlate these preliminary results with the black liquor viscosity.

5.3 Task 3 - System Modifications

During the third task, modifications were made to the existing system. Modifications included high temperature/pressure handling, flow stream heating for maintaining nominal product temperature, flow stream interface, and control and signal processing changes.

Drawings showing various aspects of the sensor are shown in Figures 3 - 7. Figure 3 shows the outside views and external dimensions of the sensor. The sensor will interface directly to the 1 inch thin wall stainless steel tubing used for the viscometer loop. Figure 4 shows similar views but also shows some of the internal components such as the magnet assembly and RF (sample) coil. Figure 5 shows the probe base footprint and two electrical signal connectors which allow for the appropriate connections to the main electronics unit which is illustrated in Figure 6. Only three of the six external electrical connectors shown in Figure 6 were used. Figure 7 shows a detailed illustration of some of the sensor internal components. The magnet pole pieces, RF coil, ceramic flow tube special stainless fittings and copper steam tube are shown.

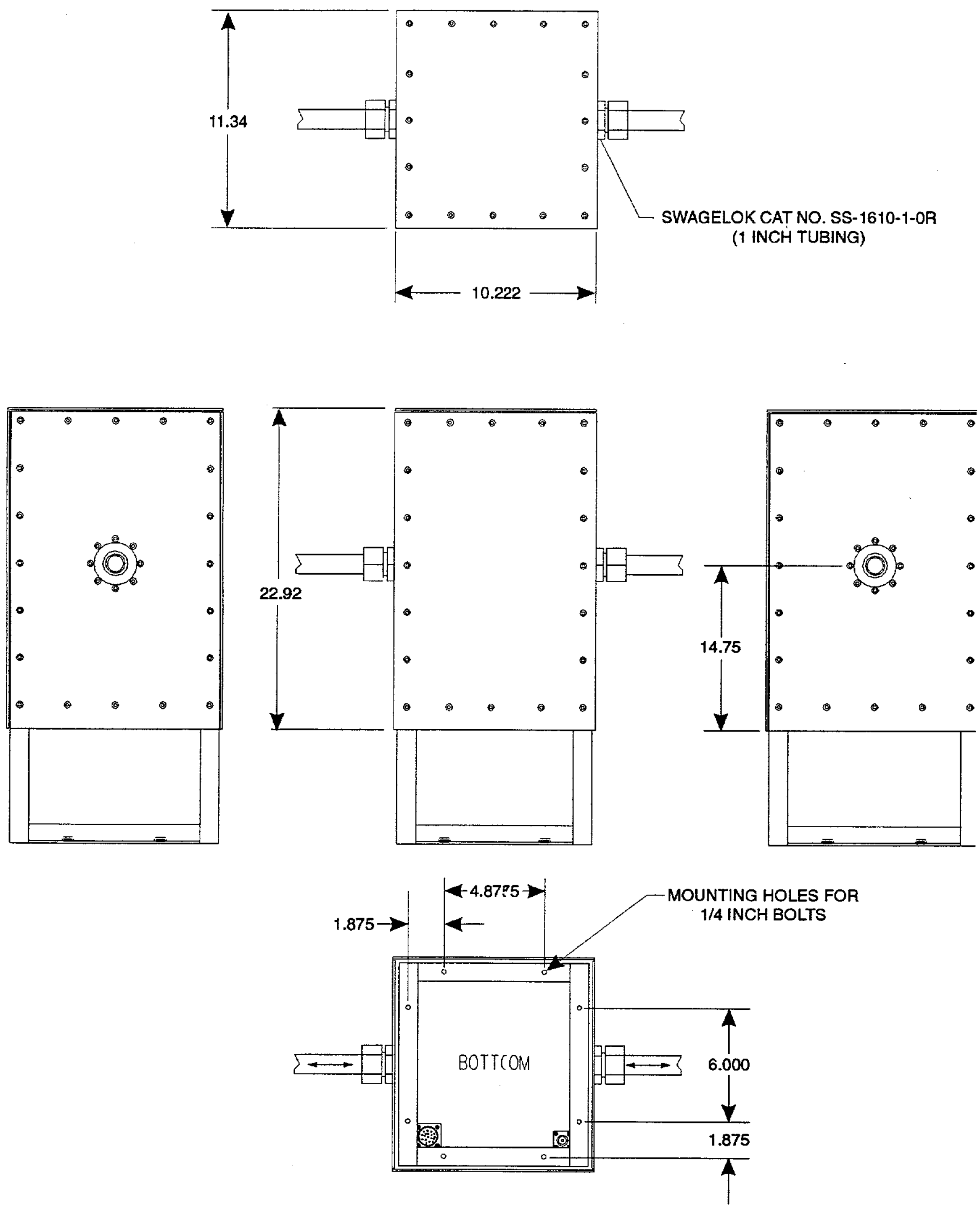

Figure 3. On-line NMR sensor showing external dimensions.

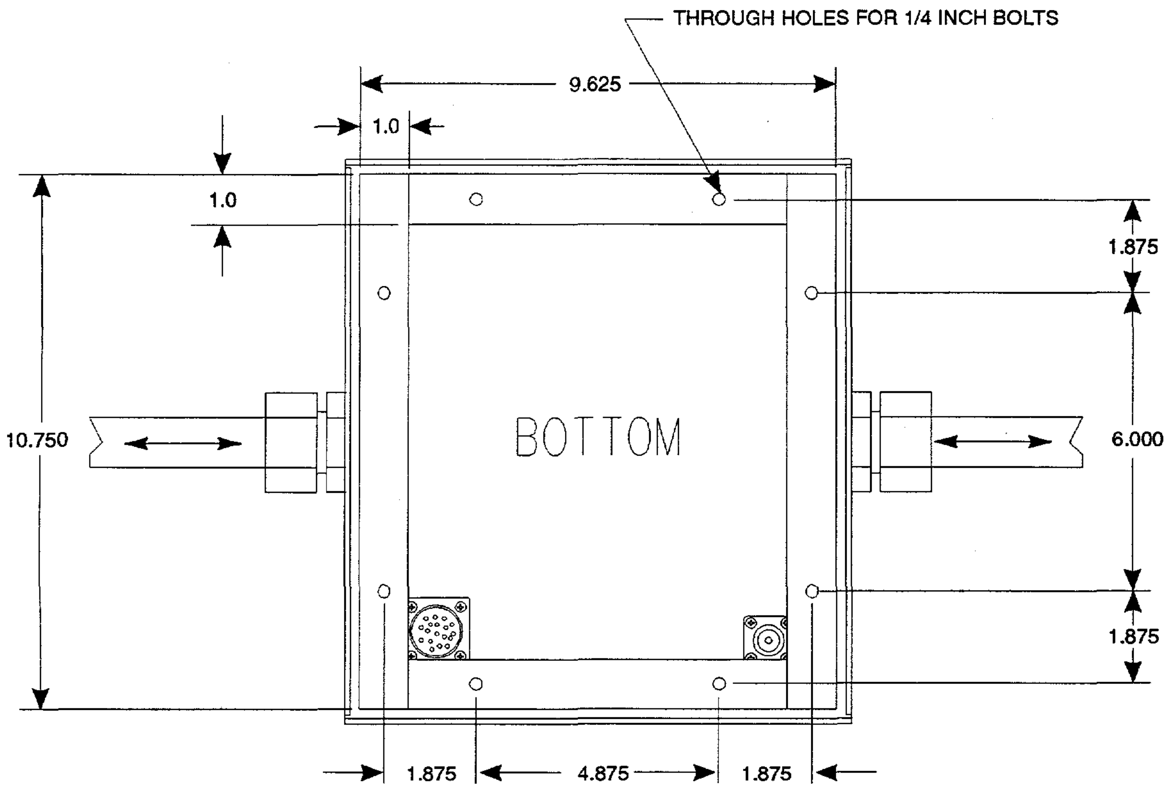

Figure 4. On-line NMR sensor showing some internal components.

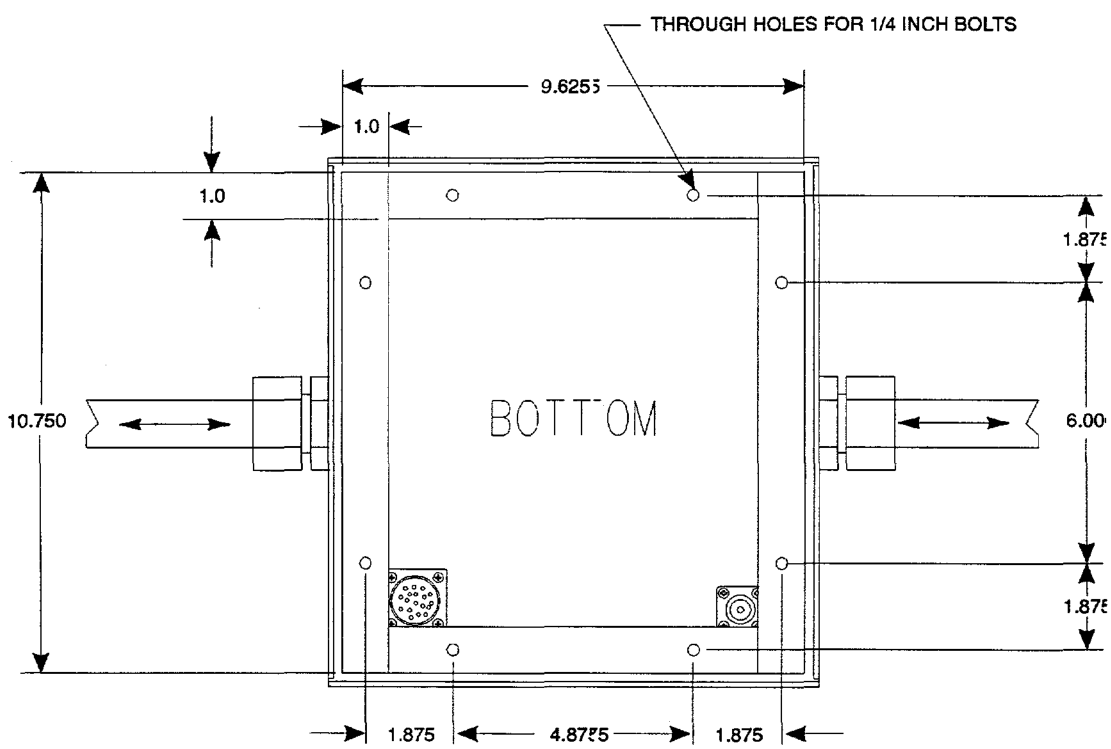

Figure 5. Sensor Base Footprint

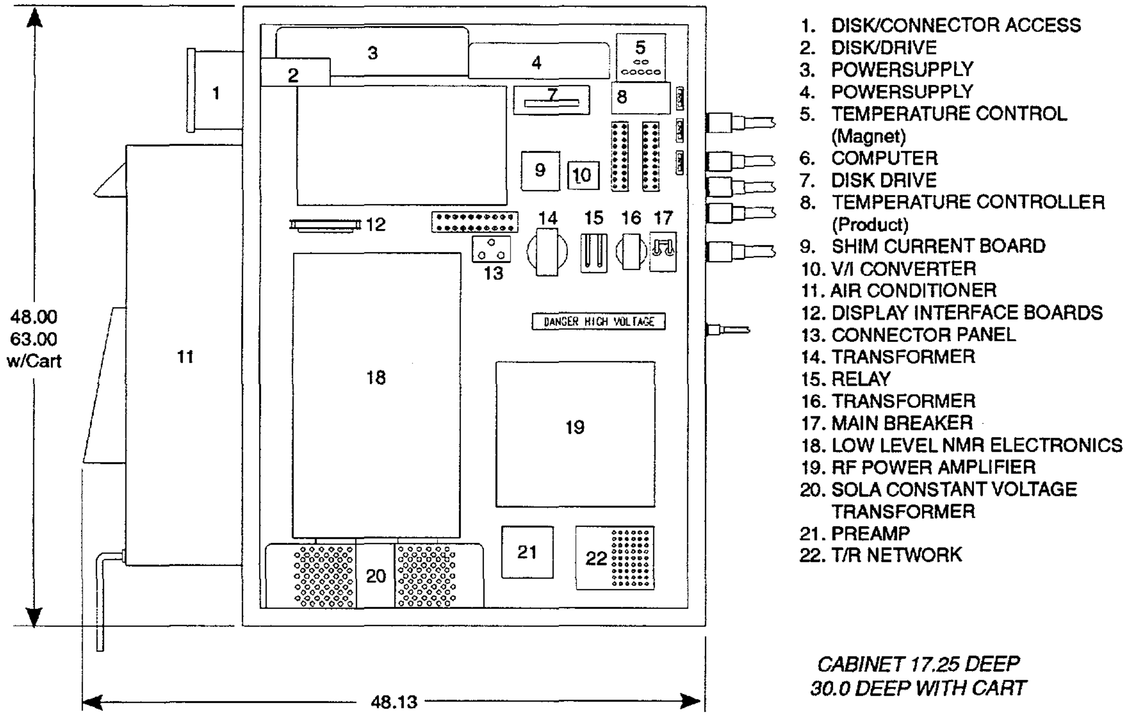

Figure 6. Main electronic NEMA cabinet showing internal components

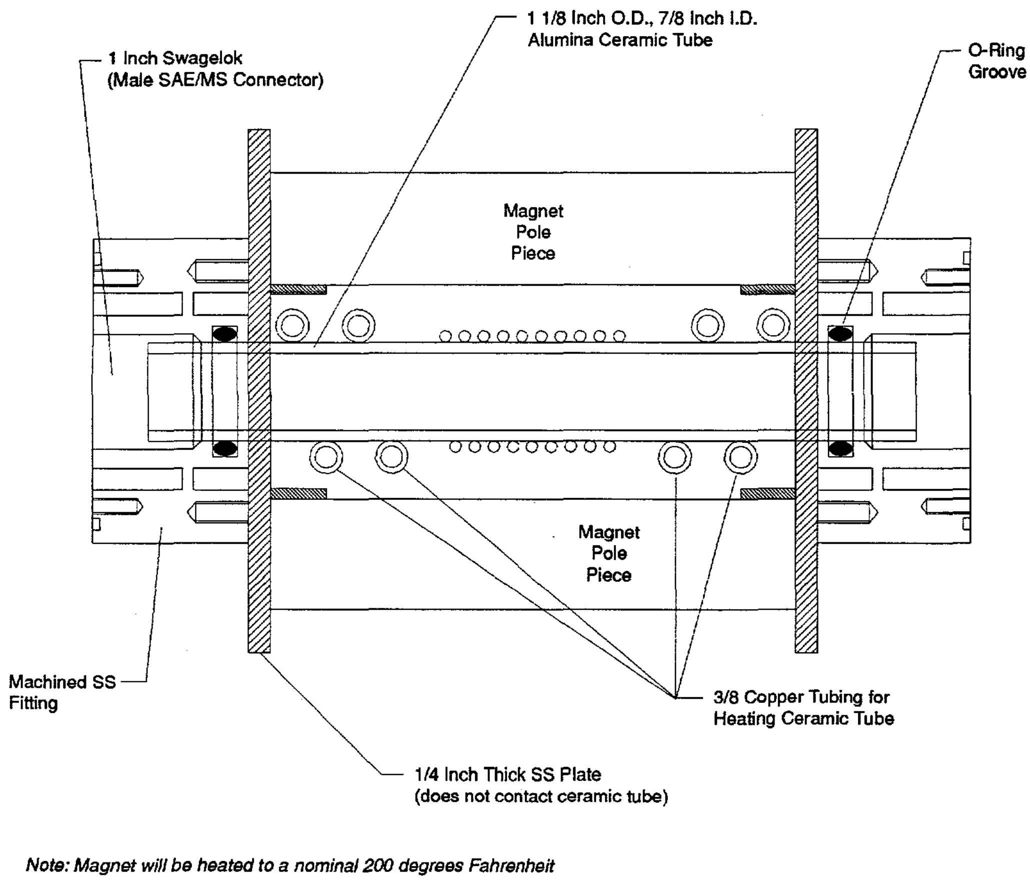

Figure 7. Details of sensor

After some testing and adjustment, the overall system operated well. Since T_1 provided the best laboratory data correlations, we wanted to implement a fast T_1 sequence to acquire more rapidly. QM provided SwRI with information necessary to perform fast T_1 relaxation time measurements utilizing a technique developed at QM. Initial results indicate that the technique is performing well but the results were not used to compute the T_1 data. Since we still had minimal experience with this sequence in this application, we decided to acquire the data and post process it. A fast version of a standard saturation recovery sequence was used to provide the data for the computation of the T_1. The system was shipped to UF on 6 March

5.4 Task 4 - Flow-Loop Tests

During the fourth task, a five-month flow loop test at the University of Florida was carried out. The modified system was installed at the University of Florida flow-loop facility and used to collect data for a period of several months. The system operated well at the University of Florida facility throughout the course of the test. The resulting data was analyzed, interpreted and compared to standard data as available. The data analysis and interpretation was primarily conducted by QM.

The system was unpacked and installed in the flow loop on 8 March. The installation went very well. With the assistance of a SwRI engineer, the system was installed on-line and operational in less than a full day. Some data was obtained the same day. Some minor software bugs were identified and fixed over the course of the next few days. The bugs did not prevent valid measurements to be made.

Some preliminary analyses of data obtained during this initial visit have been made and are described in the next section (Task 5). Due to problems with the UF data acquisition system and other flow loop issues, measurements continued through the time frame of mid-March to August.

5.5 Task 5 - Analysis and Reports

During the fifth task, the results of the flow loop tests and technical changes were incorporated into the data analysis and marketing reports. This final report summarizes the laboratory measurements, the system changes and installation, the flow-loop test results, and the market analysis.

QM developed an analysis program to automatically process the NMR data, extract NMR relaxation times and amplitudes, and correlate this data with the system temperature, solids content and viscosity. Figure 8 shows some initial results showing the dependence of the T_1 relaxation time on the black liquor temperature. The data was taken over a two day period using the same batch of black liquor. Note that for a given black liquor sample, changes in temperature correspond to known changes in viscosity. The automated analysis program was developed in anticipation of the hundreds or thousands of data sets which will be generated during the flow loop testing.

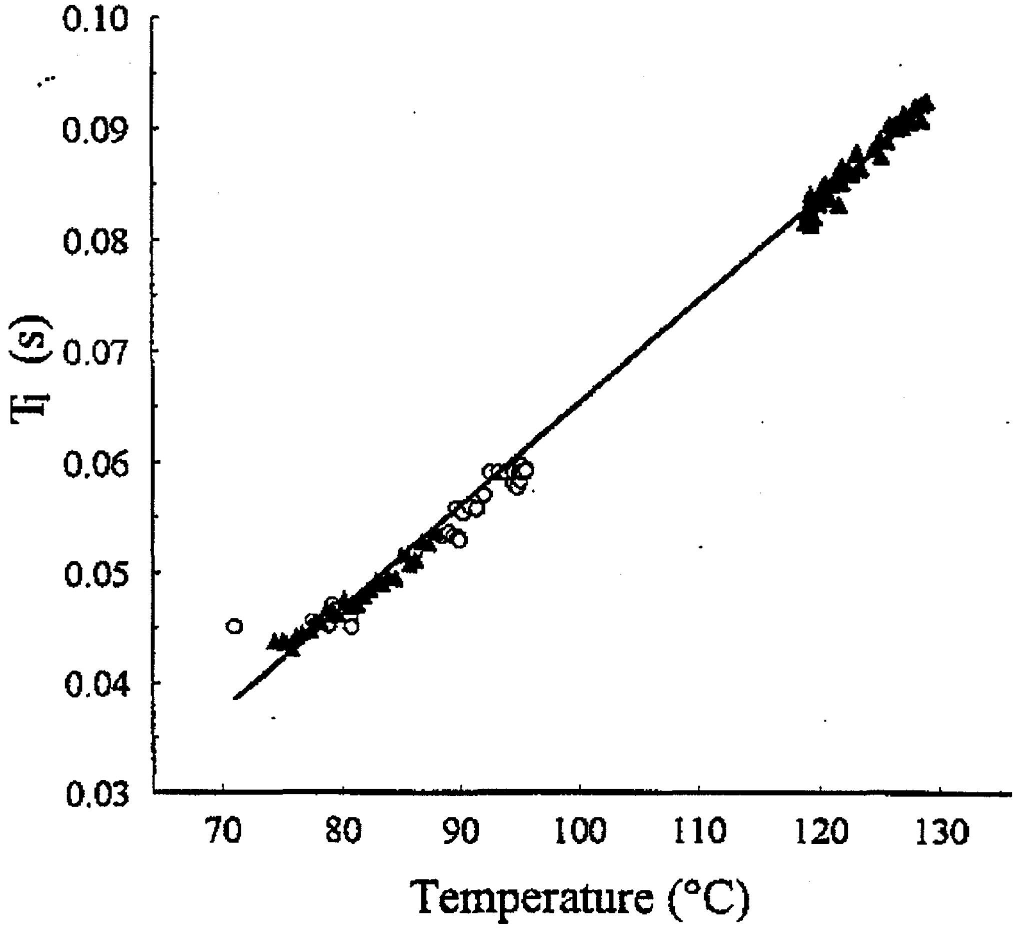

Figure 8. Initial T_1 relaxation time for black liquor plotted over a large temperature range. This data represents two days of data acquired in the first week of testing at the University of Florida. The linear fit is shown to guide the eye and does not imply that T_1 should depend linearly upon the temperature.

A total of four installments of data from the UF flow loop tests were received. Flow loop experiments have been performed on four different black liquors at varying temperatures. The standard data received from UF includes viscosity-temperature calibrations for the various black liquor samples variations in the MR parameters to the viscosity itself can be compared.

A report summarizing the field tests and data analysis is included in Appendix D.

6. CONCLUSIONS

Southwest Research Institute (SwRI) and various subcontractors, in a cooperative agreement with the DOE, developed and tested an advanced magnetic resonance (MR) sensor for several industrial applications and made various market surveys. The original goal of the program was to develop an advanced moisture sensor to allow more precise and rapid control of drying processes so that energy and/or product would not be wasted. Over the course of the program, it was shown that energy savings were achievable but in many processes the return in investment did not justify the cost of a magnetic resonance sensor. However, in many processes, particularly chemical, petrochemical, paper and others, the return in investment can be very high as to easily justify the cost of a magnetic resonance sensor. In these industries, substantial improvements in product yield, quality, and efficiency in production can cause substantial energy savings and reductions in product wastage with substantial environmental effects.

Successful tests were conducted at four different locations in the American Maize corn wet milling plant in Dimmitt, Texas. Extended field testing successfully demonstrated robustness, reliability and stability in the plant environment. The NMR sensor's electronic hardware, in itself, did not once fail or malfunction during the field test period. Software modifications were made to accommodate unusual signal conditions encountered during process startup and shutdown. Some mechanical problems were encountered with the sampling apparatus. In one case, a special sampling mechanism used only to allow a means to remove the actual samples subjected to NMR measurement for standard laboratory analysis cause a long term reliability problem. The transitions caused by this special sampling drawer allowed leakage that would have occurred in a smooth tube (cylinder). In the second case, the material was too sticky to allow long term operation without plugging. It should be noted that the plant does not try to handle this product in any conveyor.

The correlations between NMR data and laboratory gravimetric moisture measurements were quite good once problems with laboratory reference measurements were resolved. Some modifications were also made to the NMR magnet and sample coil to obtain a more rigid assembly which would not be affected by high levels of vibration encountered in the plant. Typical standard errors encountered in the corn gluten measurements were 0.3% moisture (the goal was 0.1-0.2%). Considering the accuracy limitations of the gravimetric methods and the high level of product handing and shipping delays to the point at which the gravimetric methods could be applied, the results were reasonable.

A study directed towards economic and technical feasibility of commercializing an advanced MR sensor predicted a relatively slow development of the market ($5-10M by the end of the decade).

A later application for which the system was applied to was the measurement of the rheological properties of black liquor used in paper mills. Modifications made to the system included high temperature/pressure handling, flow stream heating for maintaining nominal product temperature, flow stream interface, and control and signal processing changes. A several month flow loop test at the University of Florida (UF) was carried out. The data indicated that the MR relaxation parameters for a given black liquor correlate well with the viscosity of a given black liquor. Changes in the composition of the black liquor (e.g. the differences that exist between the Canadian Forest and Georgia Pacific black liquors) also effect the MR relaxation times irrespective of the viscosity. In other words, the MR viscometer can provide quantitative viscosity information if the nature of the black liquor is known, but the technique breaks down if there are large changes in the composition of the black liquor. The MR viscometer data is somewhat effected by flow, but these flow effects may be avoided by changing the geometry of the transmit/receive RF coil system. If the transmit coil is larger than the detection coil, then flow will cause an apparent reduction in the MR relaxation times.

In the trials conducted at UF, other viscometers produced by Brookfield Engineering Laboratories, Nametre, and MicroMotion generally measured viscosity well and demonstrated durability and reliability. In light of the performance and cost of these instruments, it can be concluded that the MR viscometers tested at UF cannot compete effectively for use as a viscometer for on-line use in black liquor recovery. If the MR technology can be used to make other property measurements such as solids content, energy, carbon or sodium content, it could be competitive at a much higher price. The potential to measure some of these parameters has been shown in other work but the tested MR viscometer was not configured for these measurements. Additional work remains to fully explore these possibilities.