WATER SOLUBLE POLYMER OPPORTUNITY IN PORTLAND CEMENT SYSTEMS

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SUMMARY

This study was requested by the Functional Polymers Group in Designed Products TS&D, for the purpose of defining the market opportunity for Methocel® and other designed water soluble polymers in portland cement systems. The project was stimulated by our interest in expanding our base in other construction and building materials in addition to paint, tile grouts, and joint cements. The basis for the findings is an extensive list of field calls on members of the portland cement industry and related end uses.

The report outlines current technology and related water soluble polymer uses in manufacturing portland cement and concrete products. The principal findings indicate opportunities for polymers which function as water reducers, pumping aids, board life extenders, fluidity aids, and workability aids.

Speciality polymers in the cost-of-use range of METHOCEL (@ $1.16/lb.) have a limited utility in most portland cement and concrete applications because of cost. The 30M lbs. of lignosulfonates used in concrete indicates a strong position secured by their low cost, favorable supply outlook and broad effective utility. They provide a valuable function without interfering excessively with the cure and strength of concrete. It is not recommended that Dow design research projects in the general field of ready-mix concrete. Pumping aids may be an exception but because of their relative high price and long-term possibility for some modest growth, however the current volume is small (250,000 lbs.) and Polox is an accepted, adequate, product. The future potential for pumping aid is estimated at 2M lbs.

It is believed that Dow water soluble polymer research could be more advantageously directed toward two other areas:

1. Water reducer, workability aid, for zero slump, "high sack content", concrete for prestressed, post tension, precast, and pipe markets; and
2. Workability aid and board life extender for prepared masonry cement.

These two represent a potential speciality water soluble polymer volume in the range of 2 - 13M pounds depending on the cost/benefit that can be realized. Both areas require the development of the appropriate new polymer as well as extensive work with concrete formulation and testing to develop the necessary technology package.

High Strength Concrete

It is recommended that Dow develop a combination water reducer, fluidity aid, and non-corrosive accelerator for the prestressed concrete and concrete pipe markets. Characteristics of the technology package needed are as follows:

1. Useful in high strength concrete (8 - 9 sacks per yard) at unusually low water to cement ratios (zero slump).
2. Provides improved workability such that further water reductions of 10 - 15% can be realized and thereby realize higher ultimate strength.
3. Provides more flexibility in choice of aggregate.
4. Developes early strength (3000 psi) in 12 hours.

5. Cost of use @ $4.00 per yard preferably but interest exists up to $8.00 per yard, depending on cummulative benefits in ultimate strength and early strength.

The estimated polymer volume potential is in the range of 1 -- 5M lbs. based on a 10 - 25% penetration.

A breakthrough in technology resulting in a 3000 psi early strength in 12 hours or less would permit prestressers to

1. Double production without further investment in "beds",
2. Reduce energy consumption for steam cure,
3. Reduce or eliminate the need for fine grind, high early strength portland cement, and
4. Reduce the sensitivity to winter temperatures.

Prestressers manufacture a highly engineered product under relatively controlled factory conditions. This situation provides a better opportunity for identifying the value of a speciality polymer than most concrete applications. The ability to pay appears present and dependent on the benefits in the additional strength attained and the labor and capital reduction realized.

Masonry Cement

METHOCEL came very close to being successful as a workability aid in masonry cement, but failed because of a price slightly out of an acceptable range and a few technical problems. A new low priced polymer at less than 2/3 the cost of use of METHOCEL ($1.16/lb. and dose of 0.07 - 0.1%) or 80¢/lb. at similar dose levels could satisfy the economic criteria of this market. A polymer potential

of 8M lbs. exists at 100% penetration if those economics were satisfied along with the following performance criteria:

- Controlled air entrainment
- Mix time insensitivity
- No excessive retardation in strength development
- Water resistant
- Resistant to grinding temperatures: 220 – 260°F

Polymer research for stucco and grinding aid applications are not recommended.

Water retention and plasticizing aids to fit the specialized technology of asbestos cement products offers an opportunity for 1 - 2M pounds of polymer as defined in the report.

MARKET SUMMARY

END USE	FUNCTION	EST. POLYMER OPPORTUNITY	COMPETITION
1. Recommended Development Activity			
Masonry Cement	Workability Aid	1 - 8M lbs.	Lime Lignosulfonates, proteins, stearates
Prestressed Concrete & Concrete Pipe	Faster early strength Higher ultimate strength	1 - 5M lbs.	None
Asbestos Cement	Water Retention Plasticity	1.5M lbs.	None
2. No Recommended Development Activity			
Ready Mix	Water Reduction Air Entrainment Pumping Air	None None 0.25M lbs.	Lignosulfonates Vinsol Resins Polyox
Stucco	Water Retention	None	
Gun Plastic	Pumping Aid	0.2M lbs.	Asbestos replacement Sample on the Shelf Products
Grinding Aid		30M lbs.	

PURPOSE

Ron Glomski and Geoff Newhouse asked for an opportunity identification study for Methocel® and other water soluble polymers in the building products and construction industry. This interest is stimulated by the expectation that the Methocel position in the paint market may erode over time because of new Dow developed thickeners. Consequently, it is necessary to direct product and applications research to new applications to assure growth in the future.

This report targets on portland cement products and systems.

METHODOLOGY

The information presented in this report was developed from field calls on many of the major manufacturers of portland cement. Field interviews were also completed with a representative sample of the following industries.

Add-mixture Suppliers
Stucco & Plaster Formulators
Asbestos Cement
Prestressed Concrete
Ready-Mix Suppliers
Concrete Pumping Contractors

A complete list of contacts is given in the appendix.

INTRODUCTION

A technology profile was attempted which would describe the current use of water soluble polymers in this industry as well as problems which could potentially be solved by using a properly designed water soluble polymer. The emphasis was directed at both processing aid opportunities as well as end use property improvers.

The primary approach was to inquire as to what industry problems existed, there relative priorities, and the associated potential value of a solution. Consequently, the report attempts to present an outside in view of what the industry currently perceives as its need for polymer additives and the economic limitations existing.

A few other problems, perhaps not related to a water soluble polymer answer, were brought out during the interviews and are briefly presented. Some may suggest an opportunity for other Dow products.

I. READY MIX CONCRETE

A. Water Reducers And Air Entrainment Aids

A high percentage of the ready mix concrete used for general construction contains water soluble polymers used as water reducers and air entraining aids. Formulated proprietary products supplied by the add-mixture firms, i.e., Master Builders and W. R. Grace, are used. A typical concrete contains 3 to 4% air and may contain 5-7% less water without change in consistancy because of the addition of this add-mixture. The cost of the average dose is on the order of 20 cents per cubic yard of ready-mix. Dose rates vary to meet the required concrete air content.

Typical products are formulations of Vinsol resin surfactants (air entrainment), lignosulfonates (water reducer), and triethanol amine (reduces the retardation effect of the lignosulfonate). These liquid formulations are added to the delivery truck by metering-dispensing equipment provided by the add-mixture supplier. This equipment is typically provided by the add-mixture supplier as part of a package deal for the add-mixture business after the fashion of the razor blade industry, i.e., give away the razor for the blade business. The add-mixture supplier's representative completely services the quipment and maintains regular deliveries via tank truck after the fashion of the residential fuel oil business. Consequently, the add-mixture business is highly service oriented.

The add-mixture product is typically around a 40% solution and sells for $1.00 to $3.00 per gallon. The ready-mix market is very cost sensitive and is satisfied with current products available. Ready mix does not appear to be an end use to be recommended for Dow water soluble product research because of the adequate performance of low cost products although a volume of around 20M lbs. is attractive.

The value of sales of lignosulfonates from pulp mills and quantities produced is shown below.

Lignosulfonates
1972 Production

	M Lbs.	Mill Value
Calcium Salt	327	2.5¢/lb.
Sodium	59	9.8¢
Other Salts	137	3.6
Total	523	3.6¢ ave.

On the order of 30 - 50M lbs. of lignosulfonates are used annually as concrete additive (~50% in ready-mix). This is about 10-15% of the production of the calcium salt. Supplies are almost unlimited. The current level of production represents only 12% of the theoretical availability from spent liquor of sulfite pulping. The remaining spent liquor is disposed of by other means such as fuel.

B. Pumping Aid

The present market for pumping aid is estimated at around a quarter of a million pounds. Its potential is on the order of ten times current consumption or 2M pounds.

An estimated 10% of the 193M yards of ready-mix is pumped, however, only the portion made from lightweight aggregate (10%) can economically benefit from a pumping aid. Hard rock concrete (90% of current pumped concrete) does not benefit sufficiently from a pumping aid.

Considerable improvements in the pumpability of concrete have been made since the early days of pumping through (1) design of the mix, i.e., selection of aggregate size and ratio, and (2) through improvements of the pumps and hose diameters. A typical pumping job is five to six floors through a 100 ft. boom of 4 - 5 inch diameter.

Pumping contractors report that Darex PA (believed to be Polyox) at $3.10 per pound is todays preferred product. The resale of Polyox by Grace at this price should be profitable. The product is reported to perform very well and the industry is relatively satisfied. A typical dose is 0.1 to 0.15 pounds per yard thus adding 30 - 50¢ to the materials cost of a yard of concrete. A typical additional charge for the ready-mix containing pumping aid is 0.50 - $1.00 per yard.

Hercules' Natrasol has generally failed as a pumping aid because of excessive air entrainment that results. Pumping aids must not affect the concrete in any way. Key criteria relative to pumping aids are listed on the following page.

1. value measured in pump maintenance savings, or
2. in its ability to keep a light weight aggregate mix from segregating
3. must not reduce concrete strength
4. must not introduce air entrainment
5. must not change set or cure times
6. should improve concrete finishing
7. should provide the concrete contractor a benefit not just the pumping contractor
8. should improve flow, plasticity, and cohesiveness
9. must be effective in a variety of mix designs and varying weight and harshness
10. easy to add and meet ASTM 494

The need for pumping aid is related to the aggregate used in the mix. Usually lightweight aggregate and coarse blend hard rock (seldom pumped) mixes can benefit from the use of a pumping aid. The future potential for pumping aid will be influenced in a positive manner by natural aggregate shortages even now experienced to a degree in some geographical regions of the U. S. An increased use of crushed aggregate will require an increase in the frequency of use of pumping aid because the angular particles (harshness) interferes with concrete flow.

The present practice for handling lightweight aggregate requires prewetting the expanded particles to completely saturate the aggregate prior to using it to prepare concrete. This step prevents the absorption of water from the concrete mix which would result in slump loss (fluidity reduction) during transit to the job site. Tempering by adding

water at the job site is to be avoided because of the variable introduced. Some pumpers claim a properly prewet lightweight aggregate mix is frequently pumped without the assistance of a pumping aid, consequently, pumping aid is not universally used even in lightweight concrete.

Perhaps the marketing of a pumping aid by Dow can best be accomplished by using an add-mixture firm such as Master Builders and Sika. The price level ($3.10 lb.) certainly suggests room for a distributor of this type. The development of a Dow marketing organization designed to sell the message to ready-mix firms, pumping contractors, concrete contractors, and building design engineering firms (material specifiers) would not appear to be advisable.

The sellection of pumping aid as a target for Dow water soluble polymer research is not given a high priority because of (1) the small market size, (2) the satisfactory performance of Darex PA, (3) the relative complexity of the possible interference with concrete properties, and (4) the probable lack of direct control of the marketing function.

II. MASONRY CEMENT

Masonry cement is a product of the portland cement industry. It is made by grinding limestone with the portland cement clinker thus it is a portland cement diluted with limestone. The product is mixed directly with sand to make mortar for various masonry applications. Masonry cement has experienced an excellent rate of growth of 6% per year during the period 1969 - 73 reaching a volume of over 4M tons. Higher construction labor cost has stimulated its use as opposed to the alternative of mixing Type I portland with lime at the job site.

Masonry cement is more profitable to the producer than portland although relative to portland it is small volume, i.e., only 4.5% of the volume. Average value of shipments in 1973 was $21/ton for portland type I versus $29/ton for masonry cement.

The mixing of lime ($21/ton 1973) with portland at the job site has been historically much larger than using masonry cement because of the lower materials cost involved. In addition, lime containing mortar has a better workability. To overcome the workability handicap masonry cement manufacturers have incorporated polymers for workability, air entrainment, and board life extension. Usually these are cheap lignosulfonates, proteins, stearate and similar products.

The opportunity for workability aids and board life extenders will be discussed in two parts: (1) standard masonry cement and (2) potential second masonry cement designed for high strength mortars.

ASTM specifications for masonry mortars define three levels of strength that may be obtained by the following mix ratios:

	Type N (750 PSI)	Type S (1800 PSI)	Type M (2500 PSI)
Masonry Cement	1 part	1 part	1 part
Portland Cement		1/2 part	1 part
Sand	6 parts	6 parts	6 parts
Alternative			
Portland Cement	1 part	1 part	1 part
Lime	1 part	1/4 to 1/2 part	1/4 part
Sand	6 parts	6 parts	6 parts

A. Type N Mortar

Although ASTM defines a strength of 750 PSI, competitive factors have resulted in Masonry cement producers designing their portland cement limestone ratio such that their product meets an internal quality control specification of 1400 PSI. So for all practical purposes, masonry cement is designed to give a 1400 PSI mortar rather than the ASTM minimum. Air entrainment must be less than 22%.

Methocel and HEC have been used by Penn-Dixie cement for a number of years in their masonry cement as a workability aid and for board life extension. Their consumption is about 200,000 lbs. annually split 50/50 between Dow and Hercules. We have been unsuccessful in developing other accounts primarily because of a high cost of use and air entrainment problems.

Medusa Cement described the following senario explaining why Penn-Dixie is unique in the use of Methocel and HEC in masonry cement. Medusa is aware of the situation because (1) of over laping market territories and (2) a plant purchased from Penn-Dixie by Medusa.

Penn-Dixie is said to have entered the masonry cement market later than others including Medusa and found market penetration difficult because their product was inferior in the mason's reaction to workability factors. To compensate and speed market penetration Penn-Dixie developed a superior handling masonry cement, however, at higher materials cost by using Methocel. They decided the cost handicap and resultant lower profit was worth the opportunity to establish an acceptable volume in the market place. So far Penn-Dixie has elected to maintain the practice of using Methocel, however, at a reduced dose. They continue to operate at a higher materials cost because of Methocel than is acceptable to the competing firms. Penn-Dixie reported that today they are under significant cost pressure to discontinue the use of Methocel in their masonry cement.

The general concensus of the attitude toward Methocel of the masonry cement manufacturers contacted is outlined below.

- high cost of use at $1.16 per lb.
- dose 0.07 to 0.1% = 6 - 9¢/70 lb. bag
- cost target < 5¢/70 lb. bag
- sensitivity to mortar mix time
- cold weather sensitive, i.e., retards set and delays early strength
- tile council patents may pertain to masonry mortars

The theoretical potential for an acceptable polymer is 8$\overline{M}$ pounds at a dose of 0.1% on 4$\overline{M}$ tons of masonry cement. Consumption of Methocel is 100,000 lbs. or 1% of the potential.

B. High Strength Mortars

Three portland cement manufacturers indicated product development activity toward a second grade of masonry cement designed for either Type S or M mortars. Masons can currently meet these mortar strengths by adding portland to the mix when formulating the mortar.

A high strength masonry cement will contain more portland and less limestone than standard masonry cement; and therefore, it will have a greater workability problem because of the increased portland content.

A high strength, prepared masonry cement would offer the advantage of convenience and better workability over a job site formulated mix, because of a workability aid polymer addition.

Ideal Cement, Peerless Cement and Leheigh are evaluating the market potential for high strength prepared masonry cement being created by an increasing trend to more highly engineered masonry. The current market is believed to be small according to Ideal Cement at less than 10% of the masonry mortar market. Portland Cement companies desire sufficient sales volume for a new cement product such that a storage silo can be turned over in a 2 - 3 month interval.

Ideal Cement reported attractive mortar characteristics in their development work at a Methocel dose level of 0.15%. At this level a cost problem exists

of 4 - 6¢/bag over their cost objective. Their target is a cost of 6¢ per bag while Methocel at 0.15% and $1.16 per lb. would cost 12¢ per 70 lb. bag. Ideal believes that at 8¢ per bag the special masonry cement would have to be priced at a premium which the market would not accept.

The market size for a workability aid polymer in high strength masonry cement is estimated to be in the range of 0.5 to 1.0$\overline{M}$ lbs. at a dose level of 0.15%.

C. Recommendations

Marketing polymers to the masonry cement manufacturers could be accomplished by direct Dow sales. It would be an excellent companion product for our developing slurry dispersant business. It is recommended that Dow develop a water soluble polymer for the masonry cement market that could be priced at a maximum of 2/3 of the Methocel price or in the range of 80¢/lb. or less assuming similar dose levels. Methocel came very close to meeting the criteria of this market but failed because of a price slightly out of an acceptable range and a few technical problems. A new lower priced polymer should meet the following:

- controlled air entrainment
- mixed time insensitivity
- faster early strength development
- water resistant
- resistant to grinding temperatures of 220-260° F
- cost of use reduced at least 1/3 vs. Methocel

The market opportunity for such a polymer is in the range of 1 - 8M pounds depending on its performance, cost of use, and dose levels.

The masonry cement end use suggests the need for two research investigations:

1. Since the product likely will be ground with the portland cement, high molecular weight Methocel as it is presently produced, may not be necessary. The relationship of molecular weight to the function of an effective workability aid requires study.

2. Should a highly sheared polymer from mechanical degradation perform the function, perhaps this suggests some process research to reach the economic criteria. The feasability of developing a low cost raw material base such as ground wood pulp to make an industrial grade low molecular weight water soluble polymer perhaps should be considered.

III. STUCCO AND CEMENT PLASTER

Stucco continues to have problems of shrinkage cracking and bonding which are associated with water retention or improper moisture levels during cure. However, the residential housing market just will not pay the premium necessary to correct these problems. Stucco is a very competitive business and, therefore, the emphasis continues to be on low cost rather than better performance.

A research product development program for water retention aids for the stucco market is not recommended. However, as products become available that are lower cost than Methocel they should be promoted by contact with the Southeast and California Lathing and Plastering Bureaus, the California Stucco Association, and local formulators in the above geographical areas. It is doubtful portland cement companies would prepare a special masonry cement designed for stucco except perhaps a white cement for the top coat only.

A. Gun Plastic

Gun Plastic is a formulated product prepared by the portland cement companies for gun application of stucco. It has contained asbestos fibers as a pumping aid to prevent the sand suspension from separating and forming plugs in the hose. Asbestos must be eliminated from gun plastic by July 1, 1976. Polymer additives have been under evaluation as an asbestos replacement.

Present alternatives are listed below.

- Lime addition will give a pumpable mix, but lime is not desirable in stucco.
- The sand ratio can be reduced from 5/1 to 3/1 but this represents a 50% increase in the cement content and the impossible cost increase equivalent to about $1.50 per sack.
- Use of a polymer additive.

To date systems based on polymer additives have been less than fully satisfactory; however, trials indicate present formulations will work. Monolith is commercially marketing an asbestos free gun plastic. California Portland and Riverside have developed formulations but haven't put them on the market. California Portland indicated their additive cost would be $1.19 per ton of gun plastic for their present developmental formulation and that Methocel is $0.50 of that. Johns-Manville, asbestos fiber supplier, reported abestos fiber cost at $2.70 - $4.50 per ton of gun plastic (asbestos @ $90/ton and dose levels of 3 - 5%); where as California Portland reported a dose of only 2% and cost at $1.80/ton.

An additive for gun plastic must meet the following criteria:

- permit pumping of a 4/1 and 5/1 mix in a 50 ft. hose
- silo and bag shelf life of three months
- resistance to grinding temperatures of 220-260°F
- a fast mix time with water
- use cost of < $4/ton over regular grind cement

The market is located in Arizona, southern California, and Florida. The polymer volume potential is small; ie. 140,000 - 280,000 pounds (dose 0.05 - 0.1%) for gun plastic but is concentrated primarily at three companies:

- Riverside Cement,
- California Portland, and
- Monolith Cement

The polymer product would be replacing 3,000 - 4,000 tons of asbestos fiber valued at $90/ton in a gun plastic market estimated at 140,000 tons.

B. Cement Plaster

Commercial buildings of block and cast concrete construction may be coated with a white cement based plaster for decorating purposes and to give a degree of water proofing. For this purpose Standard Dry Wall has developed a formulated mix containing high purity fine silica sand and calcium stearate which is capable of giving a high density compact coating. For jobs where bonding is a problem, they sell Acryl 60, an acrylic latex, for addition to the mix. Standard Dry reports a latex consumption of about 1M lbs. per year for this use. W. R. Bonsal and Penn-Crete have similar prepared products for exterior plaster.

No polymer additive, other than stearates and occasionally some latex for bonding, is used for water retention in the plaster mix. Some field problems exist due to inability to control drying rates on dry, windy days. Cellulosics have not been useful as water retention aids because of the water proofing loss that is likely.

IV. STRUCTURAL PRESTRESSED AND ARCHITECTURAL PRECAST CONCRETE

A water reducing aid effective in high "sack content", low slump, concrete suggests a potential opportunity for a polymer in the range of 1-5M pounds assuming a dose level of 0.25%. This estimate is based on a portland cement consumption in structural and architectural prestressed/precast in the range of 5.3 to 9 billion pounds and a penetration of 10 to 25%. The above polymer estimate range is sufficiently wide to include the concrete pipe market also which uses a similar concrete technology, i.e., high portland content mixes and very low water ratios to produce concrete with 28 day strengths of 5000 PSI or greater. Concrete pipe currently uses another 3.5 billion pounds of portland cement.

At the present time little or no add-mixture is used in these products for water reduction and workability aids because available concrete additives are considered ineffective in high "sack content" mixes. Placement and compaction of these low water, zero or zero minus slump, mixes are accomplished by mechanical means using vibration and mechanical compaction devices.

The interest in polymer water reducers or fluidity aids is two fold. (1) To accomplish higher strength concrete through even lower water content while essentially maintaining a current level of fluidity (producing an improved fluidity to current mixes, 5000 PSI concrete, has less economic incentive) and (2) to attempt to develop sufficient strength earlier (~ 3000 PSI in less than 12 hours) so that the "beds" can be turned over twice per 24 hr. day. Perhaps the second (early strength) can be

accomplished with the assist of an accelerator which is not corrosive to steel (which like the water reducer is yet to be invented). The prestressed industry dreams of being able to accomplish twice a day turn over. The early strength of 3000 PSI fixes the time at which tension can be released in the prestressed steel and the part removed from the bed for continuation of the development of its ultimate strength while stored in the yard.

Present prestressed concrete product yards operate on a minimum cycle of 16 - 18 hours under tension for typical products even with steam assisted cure in insulated beds. An accelerated cure time to early strength of less than 12 hours would be valuable because of increased production, better labor utilization, reduced energy consumption, reduced seasonal sensitivity, and reduced need for fine grind portland.

Prestressers can not use corrosive accelerators such as calcium chloride. W. R. Grace has introduced a product believed to be calcium formate, but the industry is not very excited about it. Sika claims a new invention which hasn't been marketed yet. Ethanol-amine reduces the retardation effects of water reducers but is not an effective accelerator.

The development of higher ultimate strength is especially valuable in column structures. C. W. Blakeslee & Sons estimated 10 - 25% of the prestressed volume could take advantage of further water reduction and resultant higher strength concrete relative to the portland cement ratio of the mix. Their target is a 15% water reduction from a current ratio in the range of 0.35 - 0.38.

Prestressers also mentioned the decline in availability of the most desirable natural aggregate. Alternative crushed aggregate with angled particles will greatly interfere with the workability parameters of a low water ratio mix. This longer range trend points toward a future need for fluidity aids to counter this potential problem. Some geographical areas of the U. S. will be sensitive to aggregate considerations before others.

It is recommended that Dow research consider giving attention to this opportunity. The technological approach through the use of accelerators and water reducers (fluidity aids) is an accepted concept of the concrete industry. Current additives used in concrete are ineffective in these unusually high "sack content", low water ratio, mixes. The market is characterized by highly engineered products produced in a controlled plant environment where it is feasable to more appropriately measure the value of a technological advance. The potential volume in the range of 1 - 5M pounds is attractive.

Initial economic considerations by C. W. Blakeslee suggest an ability to add about $4.00 to the cost of a yard of concrete. They presently are willing to look at products that would add as much as $8.00 per yard. Markets include (1) structural prestressed and post tension, (2) concrete pipe which practice essentially similar concrete technology as prestressers, and (3) to a more limited extent architectural precast.

C. W. Blakeslee and Sons appears to be a good selection to work with. They are a member of the Westinghouse

family of four prestressed/precast concrete companies with a total of eleven plant locations scattered from New Haven, Conn. to Los Angeles. They are in both architectural precast as well as structural prestressed concrete products. The Prestressed Concrete Institute represents the prestressed concrete industry membership and includes cast-in-place post tension and architectural precast manufacturers.

Marketing, most likely, would require a Dow direct approach because of the anticipated sensitivity to cost. The service requirements of the market are expected to be less than that required by the ready-mix concrete industry thus perhaps a better fit to a direct approach. Add-mixture companies may require a mark-up over our price that could put the cost of use out of an acceptable range. Perhaps using the Dow Distributors would be feasable. Further study may be required to define the best marketing approach. The bureau of census reports 293 prestress establishments reporting production.

V. ASBESTOS CEMENT

Johns-Manville defined one actual use of a water soluble polymer (extruded products) and two potential uses for asbestos cement products (wet machine process textured sheet and pipe).

A. Extruded Product (ACE)

Johns-Manville currently uses Polyox at the rate of 360,000 pounds per year. Methocel is an approved alternate. Polyox is lower cost than Methocel and is meeting the processing requirements with the exception of 3/4 x 30 inch wide flat extruded sheet. The reject rate is high in current production. Their Denver research center indicated an interest in working with Dow to overcome this problem. Perhaps this problem presents another opportunity to get a Dow designed polymer into the J-M extrusion process.

B. Wet Machine Products

Other asbestos cement products are made by a wet machine process similar to a paper machine. For example, pipe is made by rolling up a 40 mil sheet and autoclaving the wet product.

Two problem areas exist that suggest an opportunity for a polymer additive.

(1) An aid to give plasticity to a flat sheet product that is textured to a 3/8 inch depth, &

(2) A water retention aid for pipe manufacturing.

The textured sheet product cracks when a texture deeper than 3/16 inch is attempted. The volume indicates an additive opportunity in the range of 300,000 to 600,000 lbs. depending on dose level and production rates for the sheet. J-M research believes that the economics of Methocel could probably be justified. A process limitation exists in that any polymer added to the slurry in the vats must not interfere with the function of the save-all on the wet machine, i.e., ideally attaches to the solids of the mix or precipitates rather than contaminates the waste water going to the save-all.

Denver research has determined that the strength of asbestos cement pipe can be improved by a technique that (1) assures a consistantly high level of moisture in the matrix at entry to the autoclave, and (2) helps retain the water longer while the product is being cured in the autoclave. A new research project has been budgeted for 1975 to develop a water retention capability to the green asbestos cement. The time interval between forming the pipe and curing the pipe may vary enough in production such that pipe enters the autoclave with variations in moisture content which leads to strength variations. Again the addition of a "hydro-modifier" to the slurry in the vats must not interfere with the waste water save-all.

Timing would appear to be excellent to get in on the ground floor of this J-M research activity. Pipe production is about 650,000 tons annually; therefore, a polymer opportunity of 1.5M pounds may be created by a dose level of 0.1%

VI. GRINDING AID

This subject has been extensively reported on by M. B. Lellek (Report No. GHO-51, 1/31/73). The Ag-Organics Department has been selling CGA 1693 (propylene glycol) since 1971. Market entry was on the basis of a successful performance at a significantly lower price. A rapid market penetration occured in 1 1/2 years to a level of 3.7$\overline{M}$ pounds in 1972 to 28 cement plants in a market estimated at 30$\overline{M}$ pounds.

Competition didn't roll over and die, but rather reloaded with better bullets and shot back. In 1974 Dow sales have declined to the range of 1.25 to 1.5$\overline{M}$ lbs. and $170,000 profit. Ag-Organics report the business requires a lot of hand holding technical service. They presently have the business on a maintainence status with no development effort. Present contact is Gary Dalman, Organic TS&D, Freeport.

My contacts indicated that the portland cement producers are relatively satisfied with present grinding aid/pack set inhibitors. W. R. Grace has effective products and responded aggresively to Dow's competitive threat in 1972.

VII. CLINKER DISPERSANT OR SLURRY THINNER

This opportunity was not specifically covered by this market study because of our exisitng active commercial development program. However, the subject came up constantly at essentially all calls on portland cement producers. Energy cost reduction is the number one priority through out the producing industry. Active evaluation programs appeared to exist everywhere.

VIII. MISCELLANEOUS INDUSTRY PROBLEMS

The following subjects are briefly presented as they may suggest to the reader an opportunity for Dow technology or products other than water soluble polymers. The subjects were usually not a part of the study's scope but were introduced during the field interview by the interviewee for the purpose of making Dow aware of additional industry problems and opportunities.

The first two listed (dust reuse and the use of high sulfur coal) are of primary interest, and an economical solution would have a major impact on portland cement manufacturing. Both are very sensitive to manufacturing economics; however, the economic parameters can be reasonably defined.

Should the reader be interested in additional definition and analysis than presented here, please contact the author. In some cases further marketing research would be required.

A. Dust Reuse

Wet process portland cement plants waste 10 - 25% of their clinker production as dust. Dust is a partially calcined product which contains higher amounts of alkali relative to clinker. About 50% of the dust collected can be recycled in a wet plant by insufflation; however, the recycle of the remainder raises the alkali content of the resultant portland above ASTM C-150 specifications. The specification for all federal jobs is even tighter for alkali content; therefore, the dust problem is magnified when plants produce cement for federal jobs.

The value of dust varies greatly from plant to plant depending on disposal costs. Some typical economics indicate a cost of $1-3/ton to haul and throw it away by use as old quarry fill. However, this is frequently not feasable because of restrictions on ground water and the potential of the soluble alkali leaching into it. As kiln feed the dust value is around $5-6/ton or the average cost of the particular plant's raw material.

A process to reduce the soluble alkali and slurry the dust to kiln feed levels or prepare for insufflation as dust has an approximate value of $8-9/ton. Some typical plant dust volumes are listed on the next page.

	Tons/Day		
	Clinker	Dust	%
Alpha Portland			
Orange, Texas	960	225	23
Medusa			
Wampum, Penn.	2,000	291	15
Dixon, Ill.	1,750	150	9
York, Penn.	1,500	200	13
Ideal Cement			
Average			12

The portland cement industry is under ecological pressure to solve the dust problem. Disposal is not a long term solution. An economical alkali leaching or removal process is in demand. A use for the alkali leach is also a problem.

B. Impact Of High Sulfur Coal

Theoretically, from a stack gas standpoint portland cement production is an ideal industry for the use of high sulfur coal. Since combustion gases are blown through the kiln, the clinker readily absorbs the SO_3 thus stack gases can meet air pollution standards for sulfur. Plants in the central eastern states are close to Appalachian coal fields and can significantly reduce their fuel cost by using high sulfur coal.

A complication arises when high sulfur coal is used to fire the kiln. The SO_3 formed reacts with the clinker to form undesirable insoluble sulfates rather than desirable soluble sulfates. The sulfate content of portland is regulated by ASTM C-150 ($< 3.5\%$) and is normally obtained by grinding gypsum with the clinker thus delivering soluble sulfates to the portland. Gypsum addition to the grind is useful as a set regulater (retards), a grinding aid, and an optimum amount improves strength.

When high sulfur coal is burned sufficient sulfate is delivered to the cement such that the 3.5% limit is exceeded when an appropriate amount of Gypsum is added for set regulation. The insoluble sulfates, therefore, interferes with the use of desirable gypsum, and further, portland containing high levels of insoluble sulfate displays inferior strength.

The portion of the cement industry that is adjacent to high sulfur coal can economically benefit from a set regulator (gypsum replacement) that will also enhance strength in the presence of the insoluble sulfates. The estimated value of such a technology package that would permit the use of the cheaper coal is about $3.00 per ton of cement based on a $10 per ton differential in the price of the coal.

C. Pozzolanic Materials

The use of pozzolanic materials is growing in the cement and concrete industry. Fly ash and natural pozzolanic materials are being used more extensively either in portland cement manufacturing and in the aggregate mix for concrete. The reaction with typical add-mixtures for concrete is usually not positive. Perhaps the most significant interest is in aids to improve early strength.

D. Accelerators

Concrete cure accelerators are in demand which are (1) non-corrosive, (2) have less effect on shrinkage, and (3) reduce the need for fine ground portland (valued at $2.00/ton).

E. Inhibitors For The Alkali Reaction (ASTM C-150)

Portland cement high in alkali reacts with certain aggregates to produce an expansive reaction later in the life of the cured concrete. This expansion is of sufficient force to destroy the strength of the concrete. Alkali also works to the surface of wall structures to produce an undesirable white effervescence. There is also a relationship to the dust utilization problem described earlier. An inhibitor would open up new sources of aggregate.

F. Expansive Portland Cement - Type K

Shrinkage compensating cement has been available for a number of years but remains a very small volume, i.e., about 0.15% of the portland tonnage. It's a little more profitable because of its premium price of about $8/ton above Type I portland (1973 average value of shipments).

The usual concrete additives are not effective in Type K cement. There is a need for water reducing aids, workability aids, slump loss prevention aids, and set retarders that do not interfere with the expansive or non-shrinkage characteristic of the Type K cement. The needs in general are unanswered because of the small volume of Type K consumed.

G. Aggregate Problems

This subject has been handled in the previous parts of the report as it pertains to various end use concrete products. In general the availability of natural aggregate is limited and more sensitive in some areas of the country than others. The future increased use of crushed aggregate will create an expansion of the consumption of workability or fluidity aids for concrete. In addition, the growing consumption of expanded aggregate creates a dispersion stabilization problem and an increase use of polymer add-mixtures.

H. Foamed Concrete

Some research is being directed to developing a technology for foamed concrete. General Portland, Dallas, is particularly interested. Their goals

and needs were outlined as the following:

- foaming requires a "chemical" assistance
- cast in place system
- shrinkage problem during cure
- sealing and water proofing problem

I. Thin-Set Terazzo

Mortar mixes for 1/4 inch thin-set terazzo can benefit from improvement by polymer additives. Portland cement companies such as General Portland, Riverside, and Medusa make prepared dry mixes for this market. In general, polymers added to improve (1) bonding to the substrate, and (2) flexural strength of the terrazzo cause retardation of the set.

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