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# DISCLAIMER

# THE USE OF DEVONIAN OIL SHALES IN THE PRODUCTION OF PORTLAND CEMENT

by

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Abstract

The Lafarge Corporation operates a cement plant at Alpena, Michigan in which Antrim shale, a Devonian oil shale, is used as a part of the raw material mix. Using this precedent the authors examine the conditions and extent to which spent shale might be utilized in cement production. They conclude that the potential is limited in size and location but could provide substantial benefit to an oil shale operation meeting these criteria.

## INTRODUCTION

One unavoidable consequence of producing oil from the Eastern (Devonian) oil shales is the production of large quantities of solid wastes. A modest sized oil shale operation producing 10,000 bbls/day by conventional retorting of a 13gal/ton shale would produce 28,200 tons/day of spent shale. A beneficiation–hydroretorting operation operating on the same shale would produce somewhat less-approximately 13,450 tpd of tailings and 3,150 tpd of spent shale but still very large quantities.

Disposal of these quantities of tailings and spent shale in an environmentally acceptable manner represents a substantial cost burden which must be included in the price of the product oil. Conversely an economic end use for spent shale would improve the economics of oil production.

One economic use of spent shale is in the production of portland cement. There is an industrial precedent for this statement. The Lafarge Corporation uses raw Antrim shale in the production of portland cement in their Alpena, Michigan plant.

The objective of this paper is to examine the implications of that possibility as it relates to oil shale processing and to establish the conditions and limitations for the use of spent shale in cement manufacture.

## THE LAFARGE CEMENT PLANT

The Lafarge Corporation cement plant in Alpena, Michigan is today the largest cement plant in North America. The plant produces 2.0 million tons of clinker and 2.2 million tons of finished cement each year. Plant production is distributed through 25 terminals in the Great Lakes region.

The plant is located on Lake Huron adjacent to the limestone quarry which provides its primary raw material. The company quarries 3.0 million tpy of high purity limestone. Geologically the limestone is from the Alpena formation which is part of the Traverse group of upper Devonian limestones.

The second major plant raw material is Antrim shale. Some 0.7 millon tons of shale is quarried each year from an outcrop located approximately 12 miles west of the plant. After primary crushing the shale is hauled by rail to the plant site.

Operations at the plant are presented in flowsheet form in figure 1. The coarse crushed stone and shale are further crushed to 3/8", dried and blended into the raw mill. The raw stone and shale are ground to approximately 200 mesh and further mixed in the homogenizing silos.

The homogenizing silos maintain the ground raw materials in motion through the introductions of compressed air. These silos feed the rotary kiln where the raw materials react and fuse to form cement clinker. The clinker, after cooling, is ground to pass 325 mesh (44 microns) in the clinker, or finish grinding, mill. Gypsum is normally added to the finish grinding mill to control the setting properties of the finished cement. Stone is also added when making mortar cement.

Except for the use of an oil shale as a feed stock and its size, the Lafarge plant at Alpena is not unique. It may fairly be said to typify a modern efficient, dry-process, cement plant.

CEMENT PRODUCTION - GENERAL CONSIDERATIONS

A portland cement is not a simple chemical compound but rather a complex mixture of compounds and glassy phases. The compositions of the various types of cement (ASTM defines five cement types and three subtypes) fall within the following general ranges.

**Table 1. Composition of Portland Cement**

| | |
|---|---|
| CaO | 60–70% |
| $SiO_2$ | 20–24% |
| $Al_2O_3$ | 3–8% |
| MgO | 1–4% |
| $Fe_2O_3$ | 2–4% |
| $SO_3$ | 3–11% |

The raw material source of the lime is primarily high purity limestone, although in some cases argillaceous (siliceous) limestones and marble are used. Cement specifications limit the MgO content to less than five percent therefore dolomites or dolomitic limestone are not used. Silica and alumina can be obtained from quartz and bauxite respectively. Aluminum silicates however are preferred, hence, clays, shales (as at the Lafarge plant) and slates are often used. The iron content is often obtained from iron ores. Blast furnace slags, where locally available, are used as a source of all constituents.

The raw materials are blended, ground and fed to the firing kiln as a slurry (wet process) or as a fine powder (dry process). In the firing kiln where the material is heated to about 2700°F the following reactions occur sequentially:

1. Evaporation of free moisture
2. Liberation of bound water
3. Decomposition of carbonates
4. Reaction of lime with silica and alumina
5. Fusion

From these reactions it is apparent that cement making is a highly energy intensive operation. The U.S. Bureau of Mines[1] estimates that the average energy consumption in the clinkering operation is 5.6 million Btu/ton. Dry process plants are generally more energy efficient, averaging 4.8 million Btu/ton as compared with the 6.3 million Btu/ton for wet process plants.

The end result of these reactions is the formation of cement clinker. The compounds typically found in cement clinker are tri-calcium silicate, di-calcium silicate, tetra-calcium alumino ferrite, and tri-calcium aluminate. The balance among these and other compounds and glassy phases determine the end use of the cement. The composition is controlled in the blending prior to raw material grinding.

As stated earlier, cement making is an energy intensive industry. In addition to the fossil energy consumed in the clinkering operation an average of 140 kw hrs of electrical energy per ton is consumed, primarily in the raw and finish grinding.

CONSIDERATIONS IN THE USE OF SPENT SHALE IN CEMENT MAKING

A basic premise of this paper is that there may be an exploitable synergism between cement production and the production of oil from the Devonian shales. Given the prece dent of the Lafarge plant there is reason to expect that this is correct. The purpose here is to determine the conditions required and extent to which that synergism might be exploited.

The cement industry, while large, is highly dispersed. Nation wide the clinker capacity is slightly greater than 90 million tons per year. Of that total some 15 million tons are located in the states of Alabama, Tennessee, Kentucky, Indiana, Ohio, and Michigan. Using industry average figures, 15 million tons of clinker capacity would require approximately 25.5 million tons of raw material, of which, shales or clays would amount to around 4.6 million tons. This represents the maximum potential market for oil shale waste products-i.e. spent shale.

This market is currently being satisfied by various sources. Therefore a more realistic market estimate might assume a market penetration of 10 to 25 percent or a real market of 0.45 to 1.15 million tons. There are reasons to believe that this level of penetration is achievable.

Quality control is critical to the cement industry. This translates into the need for raw materials of consistent composition. I believe that the oil shales meet this criteria and it is demonstrated in the case of the Lafarge plant. Spent shales offer a further advantage over new shales in that they are dry and the water of crystallization (bound water) has been driven off in the retorting operation. This would obviate the need for drying prior to the raw grinding operation (see Figure 1) and would marginally reduce the energy consumption in the clinkering operation

The residual fuel value of spent shale may be a further incentive for its use in cement making. The spent shale from hydroretorting a shale concentrate typically contains 7-8% carbon-equivalent to about 1000 Btu/lb. Raw oil shales have a calorific value of about 2500 Btu/lb. At the Lafarge plant it is generally conceded that the use of Antrim shale reduces their total energy consumption. The extent to which the calorific value of the shale is fully utilized however, or whether it represents "idle" Btu's is uncertain. Similarly the utility of the residual carbon is spent shales must be regarded as uncertain. This is, then, a suitable topic for future research.

It is not the intent here to present an economic analysis of the use of spent shale is cement making. There are however some general conclusions which might be drawn. First, the raw materials used in cement making have a very low intrinsic value. Almost universally cement is made from locally available materials. Plant citing is normally on the basis of the availability of high calcium limestone, the primary raw material. Under these conditions the maximum value of a spent shale to the cement producer would be equal to the avoided cost of quarrying raw shale.- in the range of $3.00 to $5.00 per ton.

Spent shale has no economic value to the oil producer. To the contrary, the disposal of spent shale is an economic burden on the production of oil. Therefore a minimum benefit to the oil producer would be the avoided cost of disposal - again say in the range of $3.00-$5.00 per ton.

These two effects; the value to the consumer and the avoided cost of the oil producer, are additive. Thus the range of potential benefit to the oil shale operation would be $6.00 to $10.00 per ton.

The economic potential represented by the use of spent shale in cement making is not universally available. It can only be realized where a mineable shale exists in close proximity to a cement plant. These would however appear to be several such cases within the states where the Devonian shales are prevalent.

## Summary

From the foregoing discussion it is obvious that the use of spent shale in cement making is not an answer to all the spent shale disposal problems which a large oil shale industry might have. The potential market for spent shale is small and highly localized. However, within those limitations the economic opportunity is very real and in individual use could be very significant.

The use of spent shale in cement production should be a part of our planning and research as we attempt to develop means of economically extracting oil from the Eastern oil shales.

## Acknowledgments

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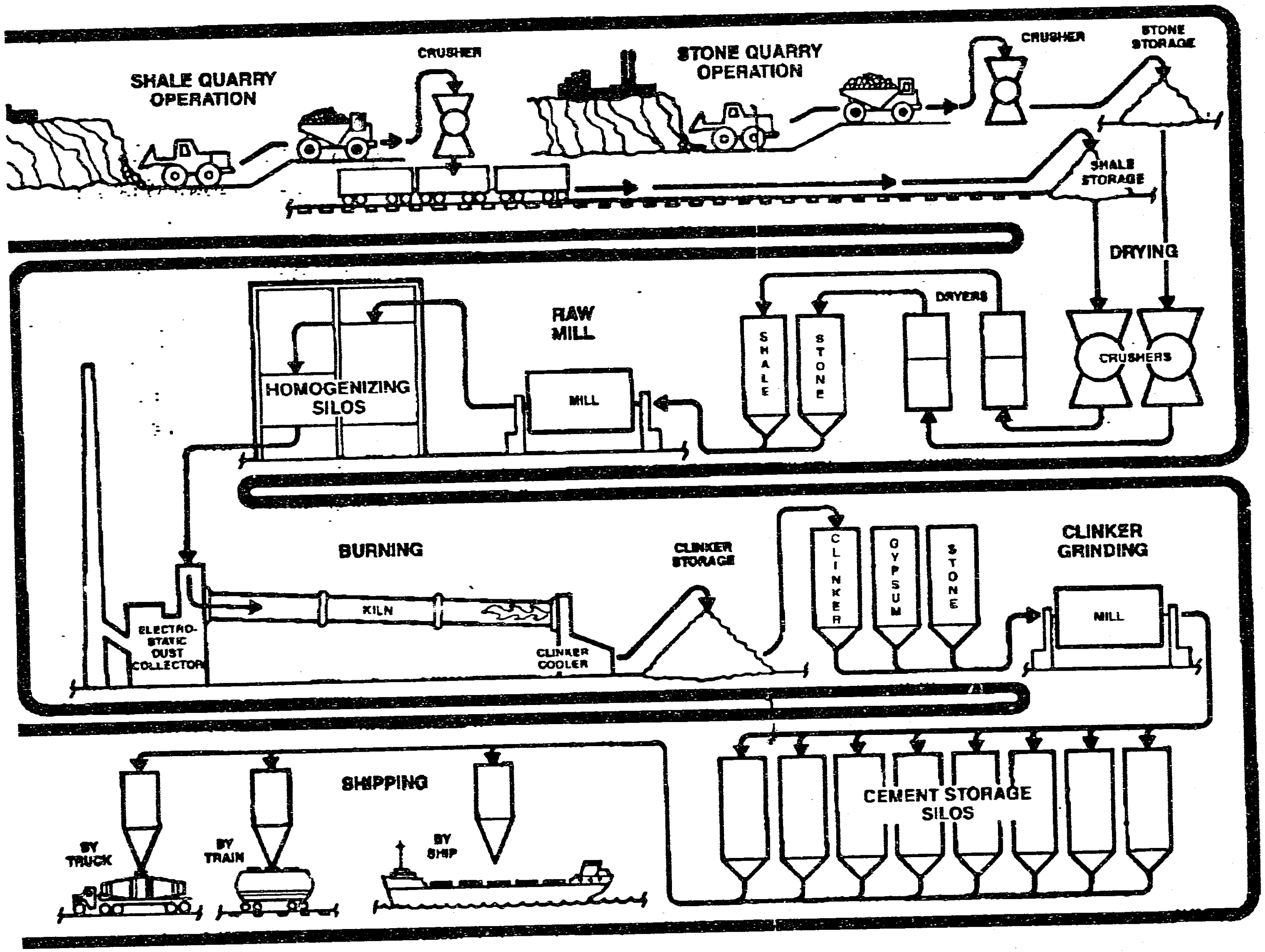


Figure 1. Flowsheet of Operations at Lafarge Cement Plant

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