LIMESTONE DEPOSITS VS. BENEFICIATION

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ABSTRACT

Limestone for portland cement must be beneficiated to produce uniform raw material for the kiln. Careful quarrying and selective recovery are factors in this process, but the chief aspects of beneficiation are "in plant" processes, such as crushing and screening, washing, grinding, flotation, and heavy-media separation. Numerous technical and economic problems exist. Detailed studies of the limestone deposit and the stone itself are required for intelligent beneficiation.

As used in this paper, *beneficiation* is defined as the improving of limestone composition so as to produce an economically usable raw material. A limestone deposit is defined as a mass of limestone which can be recovered, by quarrying or mining, for sale or for use in a commercially profitable operation. The stone may require elaborate processing, or it may qualify with little or none. Obviously, the "commercially profitable" qualification may change as the economy changes. Potentially commercial deposits may be of much better quality than actually developed deposits, and yet may be denied development for various economic reasons.

REQUIREMENTS

Limestone is discussed here primarily as a portland cement raw material, though some of the generalities can also be applied to other limestone uses.

Specifications for the various types of portland cement seem, at first glance, to be remarkably loose (see Table 1). Any attempt to demonstrate how restrictive these limits may actually be is not possible in a paper of this length. The cement manufacturer strives to achieve as uniform a raw material as is possible for each cement type; complex operational problems are more easily handled when the raw mix is uniform. Automatically, an effort is made to better the requirements imposed by specifications.

Portland cement is made through pyro-processing certain raw materials to change them chemically into manufactured compounds which may then be regarded as synthetic minerals. Chemical compositions of both raw and finished cement materials have become the language of cement technology. Detailed work on the synthetic minerals of burned cement (clinker) recently has progressed perhaps more rapidly than has investigation of the natural minerals that are introduced into the kiln. Mineralogic identity of the raw materials and the importance of their physical state (mostly fineness of grind) have for some time been recognized as significantly influencing burnability and ultimate clinker quality; however, in this field we must still rely primarily on empirical studies, with less than desirable degrees of predictability.

Cited in Table 1 are a few of the almost infinite possibilities with respect to cement raw materials. Perhaps the limestone most desirable for cement manufacture should contain enough calcium carbonate to qualify as raw material for any type of cement, when taking into account the dilution necessary because of addition of relatively small amounts of secondary raw materials. Also desirable is limestone which contains nearly the correct balance of finely divided and evenly distributed silica and alumina; however, precise qualification for one type nearly precludes qualification for certain other types without addition of secondary materials which usually are rich in iron, alumina, or silica.

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TABLE 1

Portland cement specifications and calcium-carbonate raw materials (expressed in per cent)

Generalized chemical specifications for main types of portland cement*		A theoretical raw material analysis—dry basis—for each clinker type		A possible simplified mineralogic "mix" or rock which could produce the raw material cited		Abbreviated analyses of "quarry-run" limestone known to be used for production of various cement types		
Type I:							*Ex. 1*	*Ex. 2*
Al_2O_3	Max. 7.5	SiO_2	13.7	Calcite	73.1	SiO_2	10.26	4.13
Fe_2O_3	Max. 6.0	Fe_2O_3	2.1	Dolomite	5.1	Al_2O_3	2.81	0.78
MgO	Max. 5.0	Al_2O_3	4.3	Quartz (chert)	8.4	Fe_2O_3	1.35	0.42
SO_3	2.5 to 3.0	CaO	42.5	Kaolinite	9.6	CaO	46.13	50.46
$3CaO \cdot Al_2O_3$		MgO	1.7	Siderite	2.2	($CaCO_3$)	82.11	89.76
	Max. 15.0			Chlorite	3.0	MgO	1.40	2.08
Insol.	Max. 0.75	Loss	35.2			($MgCO_3$)	2.93	4.36
Loss on Ign.						Loss	37.64	39.79
	Max. 3.0						(Clay added)	(Shale added)
Type II:								
SiO	Min. 21.0	SiO_2	15.2	Calcite	74.5	SiO_2	15.58	4.14
Al_2O_3	Max. 6.0	Fe_2O_3	2.4	Dolomite	3.2	Al_2O_3	3.18	0.21
Fe_2O_3	Max. 6.0	Al_2O_3	3.0	Quartz (chert)	11.3	Fe_2O_3	2.04	1.77
MgO	Max. 5.0	CaO	42.7	Hematite	1.5	CaO	42.48	50.16
SO_3	Max. 2.5	MgO	1.4	Chlorite	3.8	($CaCO_3$)	76.04	89.79
$3CaO\ Al_2O_3$				Muscovite	1.9	MgO	1.32	0.42
	Max. 8.0	Loss	34.9	Kaolinite	4.1	($MgCO_3$)	2.75	8.78
Insol.	Max. 0.75					Loss	35.19	41.90
Loss on Ign.								(Clay and
	Max. 3.0							sand added)
Type III:								
Al_2O_3	Max. 7.5	SiO_2	13.3	Calcite	74.1	SiO_2	13.44	0.55
Fe_2O_3	Max. 6.0	Fe_2O_3	2.0	Dolomite	5.7	Al_2O_3	4.55	0.27
						Fe_2O_3	1.21	0.18
MgO	Max. 5.0	Al_2O_3	4.0	Quartz (chert)	8.4	CaO	41.84	54.47
SO_3	Max. 3.0	CaO	42.9	Chlorite	1.3	($CaCO_3$)	74.78	97.50
$3CaO \cdot Al_2O_3$		MgO	1.5	Hematite	1.7	MgO	1.94	0.52
	Max. 15.0			Muscovite	4.2	($MgCO_3$)	4.05	1.10
Insol.	Max. 0.75	Loss	35.5	Feldspar	6.0			
Loss on Ign.				(Anorthite)		Loss	34.95	43 61
	Max. 3.0					(High calcium stone added)		(Shale added)

*Gypsum added after burning usually accounts for the level of SO_3 content—as well as for a small amount of some of the other components.

CURRENT PRACTICE

Efforts to produce uniform, specified raw material from diverse types of deposits have led to many practical solutions. Some of the approaches should probably not be included under the term "beneficiation," although the goals are the same. Currently, steps taken to improve quality may be summarized as follows.

1. Cleaning of deposit before quarrying:
   a. Stripping, by mechanical or hydraulic means.
   b. Combining this process with another recovery operation that produces usable or commercially saleable material from the "overburden."

2. Selective recovery dictated by:
   a. Variability of deposit controlled by stratigraphic changes and/or the effects of weathering (usually a factor of "vertical" significance in a deposit, unless complicated by structure).
   b. Sedimentation and life-form variations originally imposed in the environment of deposition.
   c. Structurally imposed limits; e.g. fault planes, flow thickening, overburden thickening, etc. (the latter may require underground mining).
   d. Chemical changes due to dolomitization, leaching, mineralization, etc. Recovery may be guided by three-dimensional studies of the quarry and may be accomplished by sorting of the product in the quarry.
3. "In plant" processing of stone, including:
   a. Crushing and screening—with material flow arranged to reject certain selected size grades of materials for quality reasons.
   b. Washing—with discard of selected size grades isolated usually by screening or classifiers.
   c. Sorting—varying from hand picking to elaborate recently developed photocell-circuit sorting, based on light-reflectivity properties.
   d. Grinding and classification—discard of selected size grades after sorting by classifiers is common.
   e. Flotation and concentration—following grinding and size classification, usually with a fairly complicated flow.
   f. Heavy-media (sink-float) separation—also relatively complicated and of particular interest when wide variations in specific gravity of component minerals is involved.
4. Blending is the most highly developed and widely used method of "beneficiation." A system of utilizing lime-poor limestone and upgrading it to usable quality, simply by addition of high-calcium material, achieves the same end as classic beneficiation. Important to blending systems are weighing and measuring devices working under analytical control (often with computers) in (a) windrow or other types of stacking and recovery areas; (b) dry blending and milling with blending bins; (c) wet-plant milling and slurry agitation tanks.

Improvement of quality automatically implies uniformity of distribution of components other than calcium carbonate, when dealing with cement raw materials; it also implies intimate grain-to-grain contact of fine particles. Within the prevailing practices cited above, those listed under Item 3 include the more traditional processes regarded as *beneficiation*.

THE PROBLEM—ANOTHER LOOK

More than ever, the merits of each case must be weighed. With the array of possible approaches, an important decision is when to stop the evaluation process. Needed are correct decisions regarding how much of which type of data is sufficient to justify or to reject commercial development of a deposit.

Limestone beneficiation problems have usually yielded to engineering solutions, firmly justified by a mass of chemical data. Often a plant built when economics, specifications, and reserve requirements were different, runs into quality problems with its raw materials as times change. Some solutions have been elaborate. Decisions to invest in expensive "in plant" modifications often were made when profit margins were high. Today a tough, competitive situation in the industry is getting worse.

Nearness to markets, however, may create a cost situation where "beneficiation" can be afforded. Market studies are probably given more weight than any other factor considered in plant location, and transportation costs are most important.

Some limestones are difficult to beneficiate for various reasons, most of which are geologic or physical. Among important factors are the following.

(1) *Limestone and its main products must be produced in large volume and at* low cost. Alternative sources may produce limestone that is cheaper than the cost of beneficiation. Processing of large volumes of stone requires high-cost installations and expensive processing, which cannot be afforded in many economic situations.

(2) Undesirable materials in the limestone are quite often of about the same weight as the desirable calcitic materials. In other words, it is often difficult to use heavy-media techniques to separate the desired fraction from the reject when there is little difference in specific gravity.

(3) Magnesia is undesirable and dolomitization typically alters calcite in such a way that magnesian limestones nearly defy economic separation.

(4) Limestones in many places are composed of "particles" cemented together with cement which is harder than the particles themselves.

(5) Limestones are notably subject to solution, and both solution products and grains which have been attacked by solution, create problems in beneficiation.

(6) Limestones often contain petroleum residues or other organic materials known to affect flotation, screening, milling, or related processing in an undesirable way.

(7) Silica minerals, from diagenetic cherts to precipitated quartz and sponge spicules, are complex and may create major problems for the mineral dresser.

(8) Iron-bearing minerals in limestone often are "built-in" to such an extent that processing designed to separate the iron is futile within the limits of economics. Iron is generally present in limestone in amounts higher than might be expected from casual observation.

TABLE 2

Limestone studies pertinent to beneficiation

Items to be evaluated	Studies or area of information applied to problem (no methodology)	Action indicated by studies
Weathering effect and contamination.	Study of mechanisms of weathering and the results.	Intelligent plans for stripping and quarry layout.
Effects of solution, and residual mineral materials on and in limestone.	Origin, mineralogy, petrology, and chemistry of the residual materials. Location of voids and study of voids filled from channels of streams, and of cavernous and sinkhole conditions, geodes, vugs, and porosity. Study of deposit relationship to contained and moving water.	Understanding of geologic influence of these factors on recoverable reserves, as they affect quality and operating costs.
Overburden materials, together with interbedded or structurally included rock materials.	Study of physical quarrying and handling aspects of "rotten rock," clay, and other non-limestone contaminants which must be handled in quarry operation. Finding and adequately describing the "overburden"- limestone interface and study of the reasons for its development. When "paleo-climate" weathering has affected deposit, attempt to understand why and how.	Possible use (or sale) of potential waste as "secondary" raw materials. Determination of how much non-carbonate material can be handled by existing or proposed equipment, and deciding upon which new or modified pieces of equipment may aid in handling the problems.

TABLE 2—*Continued*

Items to be evaluated	Studies or area of information applied to problem (no methodology)	Action indicated by studies
Impurities in the fabric of the limestone itself, those within individual blocks, as well as in the deposit as a whole, including impurities of both primary or secondary origin, generally "wedded" to the rock.	Detailed descriptive work on "quarry-sized" or smaller rock units with the objective of describing adequately reef features, bed continuity, facies changes, and comparable features of overall quality significance. Studies of rock features providing evidence of environment of deposition; components of the rock described and understood, with special emphasis on variability of different strata, rock fabric, cementation, crystallinity and grain size, configuration, etc. Study of the forms of silica present, geologically, physically, and chemically.	Developing plans for selective recovery where possible, including locating and adequately describing reserves. "In-plant" beneficiation planning and design of equipment and flow (included crushing, screening, and discard systems, as well as complex froth-flotation, concentration, and classification plants).
	Study of other minerals, those containing alumina and iron, sulphur and phosphorus, magnesia and the alkalies. The distribution, form, and "origin" of the magnesia should particularly be understood, if possible Analytical data should be developed for various size grades of stone produced by blasting, crushing, and milling, as well as for stone in place. Mineral-suite descriptions should include physical, mineral and petrologic information. Organic impurities and their physical implications should be recognized.	Recognition of limiting factors, which are mostly economic, with respect to beneficiation. Establishing predictability of chemical constancy and setting up procedures for checking. Understanding work index of the materials and its variability. Describing reserves in terms of chemical and physical variability range and limits—thus providing data for long-range planning.
Structure of rock in complex quarry situations.	Structural analysis of the deposits, including determination of faults and fold, controls imposed by jointing (on silicification, leaching, oxidation, etc.), and assessment of metamorphic changes of minerals insofar as possible and useful.	Appreciation of the three-dimensional aspect of the deposit; planning to follow the geologic structure where possible. Quarry planning to avoid contamination from structure where possible, and to recognize when beneficiation, underground mining, or other measures are required because of structure changes.

(9) The volume of waste in screen-to-discard systems usually is so high as to be discouraging. Sale of the rejects may provide a solution.
(10) Overburden or interbedded non-limestone materials unavaoidably brought into the plant often are so high in volume and erratic in surges as to frustrate a beneficiation system which does well on uniform feed.
(11) Complex organic-evolved shapes and surfaces of particles may present unusual problems to the mineral dresser.

LIMESTONE EVALUATION WITH RESPECT TO BENEFICIATION

Evaluation of potential limestone deposits in promising locations may be expected to indicate utilization of more limestone of marginal quality in the future. Areas of limestone once rejected may present new reasons for interest. Stone of questionable quality may not have been evaluated with respect to the possibility of applying one or more systems of beneficiation. Estimates of cost for alternatives to "in plant" beneficiation are required.

Throughout all this evaluation geological factors are so intimately involved that they must be understood and successfully handled. The mineral-dressing technologist can usually progress to a satisfactory beneficiation solution without geological advice, but the value of cooperative effort is generally recognized; geological insights may point to areas of saving.

Characteristics of limestone or of limestone deposits which are thought to be important to establishing the beneficiability of the quarry product are shown as Table 2. This table also shows methods of approach and solutions sought.

CONCLUSION

It is always possible for beneficiation of limestone to be accomplished. Whether it is justifiable, however, is a matter for economics to determine in each individual case. Development of the whole deposit as a commercial project is an involved process, so evaluation of beneficiation has to be integrated with overall plans and cost estimates. Raw-material costs should and normally can be kept low. "In plant" beneficiation usually is costly and study of alternatives which accomplish the same end is always in order.

In cases where "in plant" beneficiation is indicated, detailed study of the limestone properties should be made as part of the overall evaluation. Geologic reports of marginal deposits should include descriptive and experimental data relating to beneficiation.

Empirical approach to design of beneficiation plants not only has merit, it is unavoidable. The complexities of the problems leave no choice. The fact that each case is unique is not presented to argue against further attention to the important study of the basic parameters of limestone beneficiation.
