Sources of calcium are generally widespread and quite extensive. These sources are of limestone, dolomite, marl, chalk, and oyster shell. Cement plants account for nearly half the demand while more than two hundred lime plants in the United States and Puerto Rico consume about twenty five percent. Since the chemical composition of the limestone or other sources of calcium is critical in the cement and the lime industry, particularly for the deleterious compounds such as Na₂O, MgO, P₂O₅, and K₂O, accurate determinations are critical. Due to the tonnage per hour, these determinations must be made rapidly and accurately. X-ray fluorescence can thereby satisfy this need for accuracy and precision.

Production of lime is performed by calcining limestone and the industry is generally located and concentrated in the States of Michigan, Pennsylvania, and Missouri. The resulting product is quicklime-CaO, or hydrated lime-Ca(OH)₂. Substantial amounts of quicklime is further processed into calcium carbide in order to produce acetylene gas. In this case, the determination of P₂O₅ is critical since minor amounts of phosphorous in the acetylene gas can cause premature explosions. Other uses for lime are well known in the treatment of water, the paper and pulp industry, and the steel industry for the production of slag to remove impurities. Dolomitic lime is heavily utilized in the manufacture of magnesite refractories by reacting the dolomitic lime with brines from the Michigan basin to produce MgO and CaCl₂.

Sample preparation for these materials has been performed by grinding and pelletizing or fusion with Li₂B₄O₇. In addition to the chemistry, matrix and interelement effects will be discussed as related to the chemical analysis by X-ray fluorescence.
Analysis of any material by X-ray fluorescence is best applied to materials where the compositional range is reasonably small. Calcium/calcium-magnesium carbonate rocks fall into this category even though the calcium/magnesium ratios plus the argillaceous fractions are quite variable. In order to successfully apply an X-ray fluorescence technique, the characteristics affect the reproducibility and accuracy must be identified and corrected. These variables which can cause errors in the analysis are deviations in the particle size, mineralogy, and interelement effects due to varying chemical composition among samples.

**Particle Size**

Reproducible and accurate results by the powder method in the quantitative analysis of mineralogical samples requires proper sample preparation in order to minimize intensity fluctuations as a function of variations in the particle size and distribution. Burnstein [16] has illustrated that the fluorescent intensity from a pure material will increase as the particle size is decreased. In limestone and dolomites the intensities from several elements may all increase, decrease, or one may decrease while others increase. Campbell and Thatcher [17], measuring calcium in Wolframite where the calcium may be present as a carbonate, tungstate, or phosphate supported Burnstein's work. Differences in intensities were observed for equal concentrations of calcium in three chemical states when the particle size is large as compared to the effective depth of penetration of incident X-ray. Extensive grinding illustrated the intensities from the various mineralogical forms approach a common value by reducing the absorption within the individual particles to a small value (-325 mesh). Figure 1 illustrates the relation of intensity with grinding time or a reduction in particle for Ca-Mg carbonate rocks. Reduction in particle size causes a reduction in the intensities of iron, sulfur, and potassium while the intensities of calcium and silica are increased. As the size of the individual particles is reduced, the intensities stabilize. Further reduction in particle size through continued grinding does not promote any additional improvement in the intensities, Referring to the example on Figure 1, the minimum grinding time would be five minutes. A lesser amount of time could cause significant intensity/concentration deviations among the standards and samples. Now that a grinding time has been established, determining the proper pelletizing pressure must be determined. A similar study was performed as illustrated on Figure 2. Examination of Figure 2 reveals that in order to reproduce a consistent pellet, a pelletizing pressure of fifteen tons per square inch should be used.

**Interelement Effects**

Quantitative analysis by X-ray fluorescence of any material requires that the measured intensity of a particular element is proportional to the percent composition. A matrix such as a limestone or a dolomite
may reveal that the intensity of an element may not be directly proportional to the concentration due to result of an additional element within the sample. This non-linearity is frequently referred to as the interelement effect and may also be referred to as enhancement or absorption. When the characteristic radiation of one element excites another element, enhancement occurs. Absorption is observed when one element in the sample matrix has an absorption edge on the low energy side of the element of interest or has a mass absorption coefficient larger than the element of interest at the energy level of that element. Examples of these effects are illustrated on Figure 3 (Mass Absorption Coefficient vs Energy in KEV). Since the Si Kα line occurs just on the high energy side of the Al K-edge, secondary fluorescence will take place and conversely, silica is strongly absorbed by aluminum. A similar case is observed in the potassium-calcium System where calcium is strongly absorbed by potassium since the Ca Kα line lies just on the high energy side of the K K-edge as illustrated on Figure 3. An additional complication is the fact that iron has a high mass absorption coefficient at the energy levels of the lower Z elements, thereby acting as a strong absorber.

Although absorption and enhancement effects can be severe, mathematical corrections can easily be applied. Numerous methods have been proposed [10-14]. The author has proposed a method described by LaChance [11] where a relationship is established that the relative intensity of a characteristic line in a binary system is directly proportional to the weight fraction of a given element (A) plus (B) however must sum to unity. The expression would be as follows:

\[ R_A = \frac{C_A}{1 + C_A \alpha_{AB}} \]  

where \( R_A \) and \( R_B \) = the relative intensities of elements A and B expressed as ratios of net intensities of the elements A and B in the sample to the net intensities for the pure elements A and B

\( C_A \) and \( C_B \) = the weight fractions of elements A and B

\( \alpha_{AB} \) and \( \alpha_{BA} \) = the mass absorption coefficients of elements A and B at the effective wavelength for the excitation of the A and B radiation

\( \mu_1 \) and \( \mu_2 \) = the mass absorption coefficients of elements A and B at the effective wavelength for the excitation of the A and B radiation

\( \theta_1 \) and \( \theta_2 \) = the angle of incidence of the primary X-ray beam and the take off angle of the secondary radiation

Calibration of the standards involves an iterative process according to Equations 3 and 4 which establishes the a coefficients which are then assigned to Equations 1 and 2. The unknown sample data is then processed through multiple regression analysis utilizing Equations 1 and 2.

**Sample Preparation**

As previously discussed, particle size and distribution can have an effect on the intensities of most elements with the most severe being at the low Z end of the periodic table. An illustration of this fact, Figure 1, displays the effect of grinding time translated into smaller sized particles with increased grinding time. Eight (8) separate samples of single standard of five (5) grams and 0.1 grams of Na-stearate as a grinding aid were placed in a tungsten carbide rotary swing mill and ground for one (1) to eight (8) minutes. The resulting powder was then pelletized under 15 tons per square inch with boric acid as a backing material. Each pellet was analyzed with the resulting intensities plotted as a function of grinding time (Figure 1). The grinding curve indicated a minimum grinding time plus one (1) minute for a total of six (6) minutes.
Instrumentation

A Rigaku RIX 3100 X-ray spectrometer with a 4 kW generator was utilized for this analysis and was operated under the instrumental operating parameters as described on Table 1.

Results and Conclusions

The samples utilized in this study were seven (7) standards supplied by the National Bureau of Standards [18], Ash Grove Cement Company [19], Hercules Cement Company [20], and well characterized unknown samples from Medusa Cement Company [21]. The standards and unknowns were derived from diverse geographical and geological areas. In addition the mineralogical structure varied from calcite (rhomboidal-R-3c), vaterite (hexagonal-P63mc), aragonite (orthorhombic-Pnm), and aragonite (orthorhombic-Pmca) as listed in appendix A. The results of analysis is contained on Table 2, while the individual calibration curves are contained in appendix B. A typical spectra of limestone is contained in appendix C.

The results of analysis contain Table 2, while the individual calibration curves are contained in appendix B. A typical spectra of limestone is contained in appendix C. Calcium oxide and magnesium oxide, the main components in Ca/Mg carbonate rocks, exhibited absolute errors of approximately two to four percent relative utilizing a simple least squares regression analysis. Utilizing the theoretical alpha routine as outlined by LaChance [11] with a multiple least squared analysis, these errors were reduced to 0.07 and 0.05 percent respectively. It should be noted that the CaO in the unknowns was initially determined by a KMnO₄ titration with no attempt to differentiate between CaO and SrO. In the KMnO₄ titrimetric determination of CaO, both the CaO and SrO are both precipitated as a calcium-strontium oxalate and when titrated with KMnO₄, the oxalate ion is being determined. As a result, the determined value by this method will be CaO plus SrO. In a limestone or a dolomite, the SrO could be from 0.05 to 0.3 percent. Therefore, since X-ray fluorescence determines CaO and SrO separately, the SrO and CaO determination by X-ray fluorescence must be combined in order to agree with the KMnO₄ titrimetric calculation.

Conclusions

The results of analysis illustrate that X-ray fluorescence is a viable technique for the analysis of limestone and dolomite. It further illustrates that, with proper sample preparation, mineralogical differences become insignificant. Data reduction the use of theoretical alphas automatically solves the problems associated with absorption and enhancement effect.

References


Hooper, P. R., "Rapid Analysis of Rocks by X-ray Fluorescence", Analytical Chemistry, 36, 1964.


Burns, F., Particle Size and Mineralogical Effects in Mining Applications of X-ray Analysis, Denver Research Institute, University of Denver, 1962.


National Bureau of Standards, Washington, D.C.

Ash Grove Cement Company, Kansas City, MO.

Hercules Cement Company, Bethlehem, PA.

Medusa Cement Company, Dixon, IL.
### Appendix A. Listing of Standards and Source

<table>
<thead>
<tr>
<th>STD</th>
<th>GEOLOGIC FORMATION</th>
<th>REGION</th>
<th>SOURCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-1</td>
<td>Burlington</td>
<td>Missouri</td>
<td>Ash Grove Cement Co.</td>
</tr>
<tr>
<td>LS-2</td>
<td>Raytown</td>
<td>Kansas</td>
<td>Ash Grove Cement Co.</td>
</tr>
<tr>
<td>LS-3</td>
<td>Squamish</td>
<td>British Columbia</td>
<td>Ash Grove Cement Co.</td>
</tr>
<tr>
<td>LS-4</td>
<td>Kimswick</td>
<td>Missouri</td>
<td>Ash Grove Cement Co.</td>
</tr>
<tr>
<td>LS-5</td>
<td>Jacksonburg</td>
<td>Pennsylvania</td>
<td>NBC</td>
</tr>
<tr>
<td>LS-6</td>
<td>Jacksonburg</td>
<td>Pennsylvania</td>
<td>Hercules Cement Co.</td>
</tr>
<tr>
<td>LS-7</td>
<td>Farley</td>
<td>Nebraska</td>
<td>Ash Grove Cement Co.</td>
</tr>
</tbody>
</table>

### Appendix B. Typical Limestone Spectra

[Graphs showing typical limestone spectra]