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31-36

MODERN TOOLS OF CERAMIC RESEARCH

by

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Within the past thirty years increasing use has been made of the modern instruments of research in providing some of the missing links in the study of the raw materials and products of the silicate industries. This has meant the constant cooperation of engineers and physicists in developing new equipment, and also the cooperation of research personnel in such fields as soil science, ceramics, mineralogy, and chemistry, in making evident the need for such equipment and in developing techniques for the solution of ceramic problems. The net result has been new and better products and methods of manufacture, more accurate control of materials and processes, a greater insight into the silicate minerals and all that occurs in their evolution from the mine to the market, and the laying of the groundwork for future ceramic discoveries and improvements.

Ceramic materials possess a remarkable and variable combination of properties. Silicon, next to oxygen, is the most abundant element in the earth's crust and in nature is always found in the combined state. Clay, which is one of the most important constituents in soils, is composed of one or more of a group of complex silicates called the clay minerals. It is also the basic ceramic raw material. Clays are secondary products and are found in varying stages of alteration. They possess colloidal properties and are of extremely fine particle size. In nature they are found to be impure to a greater or lesser degree and have a variable chemical composition. The crystal structure of the clay minerals is complicated. When clays are wetted, they develop plasticity, which allows them to hold their shape when they have been deformed. They may be fired to controlled high temperatures and will then undergo changes in crystal structure, physical properties, and chemical composition without alteration of the formerly plastic shape. The usefulness and the large number of different types of ceramic products are dependent on these properties, but because of them it is little wonder that some of the advances in the basic studies of ceramic technology were required to wait for the twentieth century and its progress in instruments of research.

The polarizing microscope, the spectrograph, x-ray diffraction apparatus, and differential thermal analysis apparatus have shed much light on the subject of ceramics. Their importance in such diverse enterprises as the glass, porcelain enamel, dinnerware, insulator, portland cement, and clay mining industries may best be seen by a short discussion of some of the specific problems in which they have played a primary role.

The description of apparatus must be confined to general principles and the bibliography at the end of the paper contains references which may be consulted for further information.

The Polarizing Microscope

The polarizing microscope is "an optical instrument consisting of objectives and an eyepiece that magnifies minute objects for visual observation or photographic record by direct illumination and in which the object is on a rotating stage between crossed Nicols."[1]

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There are two Nicol prisms in a polarizing microscope. The first is called the polarizer and it is located below the stage of the microscope. The polarizer resolves the light passing through it so that it vibrates in one direction only, producing what is known as plane polarized light. The second Nicol prism is called the analyzer and it is located in the body tube of the microscope above the objective. When the optic plane of the analyzer is perpendicular to the optic plane of the polarizer, all the light is rejected and the Nicols are said to be crossed. The analyzer may be removed from the body tube when it is not in use. The rotating stage is graduated in degrees and acts as a mount for the glass slide containing the specimen to be observed. It allows the specimen to be rotated for the determination of extinction angles, interference figures, and other optical data. There are many types of objectives which vary in magnifying power and in the ability to correct for aberration. The objective consists of a group of lenses which form a real image of the specimen. This real image is later magnified by the eyepiece. The ocular often corrects for aberration in the objective. The Huygenian eyepiece is commonly used in many microscopes and consists of two plano-convex lenses, the upper lens having a focal length about twice that of the lower or field lens. These lenses are mounted and may be removed from the body tube when desired.

Probably the most important use of the polarizing microscope is for the identification of minerals and other crystalline materials. With special techniques it may be used to determine the strain in glass, the constituents of portland cements, and much other information which is of value in both basic research and plant control. Some of these methods will be discussed in the following cases.

Case 1. The great variation in the composition of clay in a single deposit has been known by clay producers for a long time. V. T. Allen[2] made a study of clay samples which were obtained from many different sections of the United States and with the microscope showed that the clay minerals (of which there are a large number) and other hydrous aluminum oxides are capable of migrating through a deposit of clay after that deposit has been altered from the original rock. Cracks in the deposit and the circulation of water with good drainage are held partly responsible for this. Microscope slides showed such things as veins of white montmorillonite cutting gray or buff montmorillonite, the filling of bubbles in bentonite (originally found in the parent volcanic glass) with montmorillonite, the filling of a fracture zone in kaolinite with nontronite, and the presence of kaolinite veins in an altered porphyritic rock. The application of such a study may be of great value in providing more uniform clays to industry, and eventually in eliminating many of the plant troubles caused by variation in clay deposits.

Case 2. Awareness of the variation in the composition of similar clays of a certain region was brought about by a study of Georgia kaolin.[3] The microscope was used to examine a number of clays from the mines along the Georgia Fall Line. This information as well as that obtained by x-ray and thermal methods indicated that variation in the degree of development of kaolinite was the most important factor in causing the difference in properties of the kaolins of this region.

Case 3. The microscope has been helpful in studies pertaining to phase diagrams. These diagrams are very important to the ceramic technologist, for they tell much about the chemical and physical reactions which occur in mixtures of materials at high temperatures. Briefly, a phase diagram is "a graph showing the relation of one or more properties of one or more substances."[4] There are several types of phase diagrams, but the forms most used in ceramics are obtained by identifying the phases (gas, liquid, or solid) which are encountered when percentage composition and temperature are varied. For example, in studying the system magnesium oxide-boric oxide[5] all the phases which were obtained with different combinations of magnesium oxide and boric oxide were examined with a petrographic microscope, and thus were identified. Such information is of importance in the development of boron glasses and glazes and in some cases anomalies in plant practice may be explained.

Case 4. The most important defects in glass are stones, which are unmelted inclusions in the glass; cords, or striae; and bubbles. A study was made of most of the types of glasshouse stones found under operating conditions in a glass plant.[6] At least fourteen different types of stones were found and identified with the petrographic microscope. Contamination by refractories and metal parts of the tank, incomplete solution of some of the material in the batch, incorrect composition of the glass, improper viscosity of the glass, incorrect furnace design, and surface volatilization were found to be some of the causes of glass stones. When so many factors influence the final glass product, constant control of methods and materials is essential in those industries which demand a non-defective glass. Hence, application of petrographic information may mean dollars and cents to the plant owner or stockholders.

Case 5. Cords or striae often produce excessive stresses which may greatly weaken the final product. For this reason the Glass Container Association of America developed a method for determining the strain in glass by means of the polarizing microscope.[7] In practice, the examination of one container every twenty-four hours was recommended. This procedure is believed by the Association to be capable of checking cord defects before too much loss of ware has taken place.

Case 6. In the past great losses have been sustained by the porcelain enamel industry because of defects occurring during the preparation, the application, and the firing of the enamel coating on steel. Tearing of the enamel, which usually occurs in the firing process, is caused when the enamel cracks in drying and pulls away along irregular tears. The preparation of thin sections of enamel specimens were studied, and striking differences were observed between enamels which tear and those which do not tear.[8] The causes and some remedies for the tearing of enamel were determined. This is another example of the application of fundamental research to industrial practice.

The Spectrograph

Although the spectroscope has been used for the identification of elements since 1860, it is only within the past twenty years that it has become one of the foremost analytical instruments. A spectroscope is "an instrument for analyzing light by separating it into its component rays."[9] When a spectroscope is equipped with a recording device (usually photographic) to obtain a permanent record of the image of the spectral lines, it is known as a spectrograph.

When a substance is appropriately heated, its vapors give off light which is characteristic of the metallic elements present in the material. It is this light which is separated into its components by a prism or a grating. When this light is photographed, the resulting picture consists of a series of lines, known as a bright line emission spectrum, which make it possible to identify the substance. Although other types of spectra are commonly used, the discussion will be confined to the bright line emission spectrum because it is of the greatest importance in analytical work.

The principal parts of a spectrograph are (1) an excitation source for vaporizing the material to be analyzed, (2) a slit, which acts as a narrow aperature and new source of light, (3) the lenses, which render the light rays parallel, (4) the dispersing system (prism or grating), which separates the light into its component rays, and (5) the recording system, which provides a permanent record of the spectrum.

The spectrograph has the advantage of making possible very rapid qualitative analyses of a great many elements and of the accurate quantitative analysis of minute traces of elements in a material. Only a small amount of sample is required and the sensitivity in most cases is very great. The spectrograph has brought about a saving in time and has made possible the determination of minute amounts of rare elements which ordinarily would be overlooked by other methods. The descriptions which follow demonstrate the adaptability of the spectrograph to a wide range of problems.

Case 1. A study was made some time ago of the effect of glass on alcoholic products stored in bottles at room temperature for three years.[10] The sensitivity of the spectrograph was responsible for the detection of small amounts of silicon, aluminum, and magnesium in the alcohol product which had been so stored in certain types of the glass containers. No contamination of the alcohol occurred when the alcohol was stored in Pyrex brand bottles. This work very ably demonstrated the possibilities for the superior storing of alcohol products over a long period of time.

Case 2. There has been much controversy over the degree of the effect of alkalis in portland cements. Belief that the presence of the alkalis in excessive quantities was detrimental brought about rigid specifications concerning the allowable amounts of alkalis in portland cements. This means that all portland cement which is used must be analyzed for the alkalis. Very recently a spectrographic procedure for the determination of sodium, potassium, and lithium in portland cements was developed by Armin Helz.[11] He states, "The procedure is rapid, requiring about 4 hours for the determination of sodium and potassium in six samples as compared with 30 hours for the chemical procedure." Where a large number of analyses are to be made, the spectrograph is a source of great saving in time.

Case 3. Increasing interest in trace elements in materials has been shown in recent years. In some cases very minute quantities of an element may have a tremendous effect on the properties of a substance. For this reason the spectrographic method was applied to clay analysis. A procedure was developed for the determination of trace elements in clays.[12] Such an analysis would not have been tackled by the ordinary chemical methods. The development of such procedures indicate the possibility of more stringent control and more uniform products in the future.

X-ray Diffraction Apparatus

The story of x-ray analysis is a short but brilliant history, for x-rays were first discovered by Wilhelm Roentgen in 1895. Although observations and discoveries were made as early as 1705, Roentgen was the first to announce the existence of x-radiation. X-ray analysis by means of powder diffraction methods has established many facts concerning the structure and the identification of ceramic materials. The future application of x-ray analysis is apparently unlimited and its value in research and plant control is inestimable.

X-ray analysis concerns "the determination of the internal structure of a material by means of the diffraction pattern formed when an x-ray beam passes through it."[13] At first only single crystals could be studied, but Debye and Scherer in Europe and Hull in America independently discovered a method by which a powder could be identified by x-ray analysis. Through this discovery the application of x-ray analysis to ceramic problems was inevitable, for ceramic materials are seldom, if ever, found in sufficiently large crystals to adapt them to a single crystal method.

The principal parts of the apparatus used in x-ray analysis are (1) the x-ray tube with transformers and electrical equipment to produce x-rays, (2) a camera with a collimator, (3) a mounting for the sample within the camera, and (4) a film for recording the x-ray diffraction pattern. The film is placed around the inside circumference of a cylindrical camera. The powdered sample is placed in a straw or capillary tube and this container is mounted vertically in the center of the camera. The collimator is made up of two lead pinholes which receive the beam of x-rays. When the x-rays enter the camera through the collimator, they impinge on the sample and are diffracted by the crystal powder. The diffracted beam is recorded on the photographic film and this picture reveals the structural arrangement of the atoms in the crystals of the material.

Case 1. X-ray diffraction methods as well as the petrographic microscope have been widely used in the work on phase diagrams. X-ray diffraction data were determined for compounds in the system $CaO-MgO-SiO_2$.[14] This fundamental information may be correlated in other research projects concerning the calcium and magnesium silicates. The x-ray diffraction apparatus and the microscope have been mainly responsible for the vast amount of phasé diagram work that has been done in recent years. Such work has aided the ceramic engineer in the preparation of better products.

Case 2. X-ray diffraction methods may be used in many ways in manufacturing control. F. G. Firth of the North American Phillips Co. has discussed a number of these applications,[15] among them the use of x-ray analysis in determining particle size, in determining the constitution of fire glaze products in refractories, in predicting crystalline changes which occur during the firing of ceramic products, and in controlling the transformations which occur in the firing of steatite insulators.

Differential Thermal Analysis Apparatus

Differential thermal analysis is another method for determining the character of materials where the microscope, chemical methods, and x-ray analysis may not always be used. When certain minerals are heated, chemical and physical changes occur which are exhibited by exothermic (liberation of heat) and endothermic (absorption of heat) reactions. A standard material (usually alumina) and the material being tested are heated simultaneously and the difference in their temperatures is measured with a differential thermocouple. The rise of temperature in the heating chamber is also measured. This information is plotted to form a curve which is characteristic of the mineral being investigated. These curves have been very useful in identifying the clay minerals and other hydrous aluminum oxides.

Case 1. R. E. Grim has suggested the differential thermal analysis apparatus as a control and prospecting method.[16] It has been possible to predict the properties and potential uses of clay deposits, and a correlation of the thermal analysis data with ceramic properties was shown to be very practical. The material from several refractory and face brick plants was studied and variations in the clay deposits which are responsible for variation in the final product were detected. Although the method is a rapid one, much preliminary work would be necessary to apply the findings to control work. In a large plant such preliminary work undoubtedly would be worth-while.

The use of modern instruments in solving ceramic problems has been the foundation for many new ideas in a large and expanded industry. These instruments have not become a substitute for the older methods of analysis, but they have augmented the value of these more common methods by increasing the range and scope of research and control. The importance of the modern tools of research is undisputed. Without a doubt the future of ceramic technology will continue to be more dependent on its allied fields of physics and engineering. The result can only be a continued progress with an increased tempo in knowing more about these complex silicates which surround us in everyday life and in the production of new and better articles at a lower cost than ever before.

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O & C LANDS

On May 22 Senator Cordon sent the Department the following telegram:

> SUB-COMMITTEE ON SENATE PUBLIC LANDS COMMITTEE ON SATURDAY FAVORABLY REPORTED TO THE FULL COMMITTEE S. 723. THIS BILL CONTAINS PROVISIONS FOR RESTORING O AND C LANDS TO MINING ENTRY. HOPE TO OBTAIN ACTION BY FULL COMMITTEE IN NEAR FUTURE AND SHALL KEEP YOU ADVISED.

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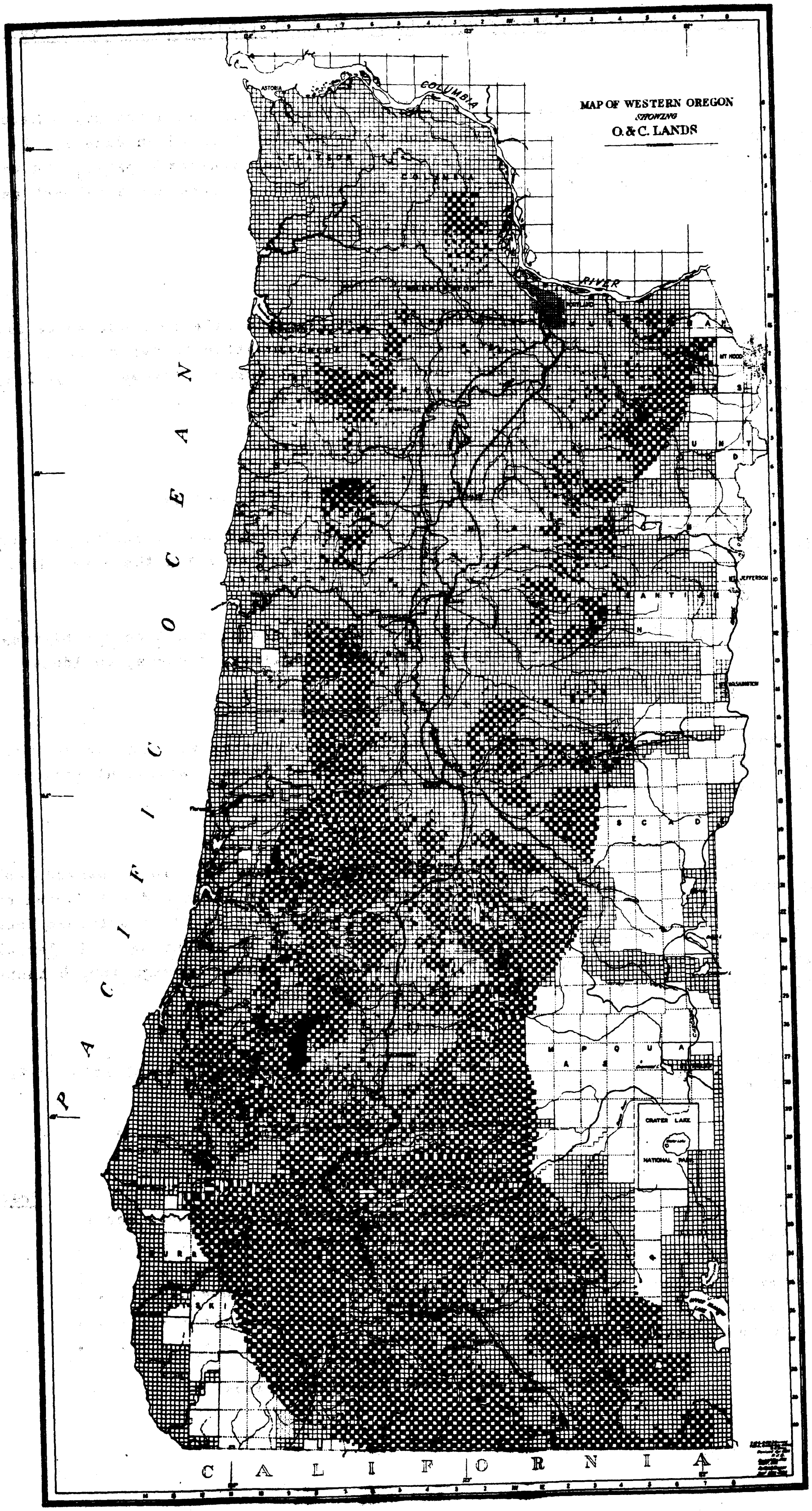
MAP OF WESTERN OREGON
SHOWING
O. & C. LANDS
COLUMBIA
RIVER
ASTORIA
MT HOOD
MT JEFFERSON
CRATER LAKE
NATIONAL PARK
P A C I F I C O C E A N
C A L I F O R N I A

MINING CONVENTION

The Jackson County Mining Association and the Siskiyou Mineral Association have announced plans for the Western States Mining Convention to be held at Medford on June 13, 14, and 15. Speakers will discuss problems concerned with price of gold, venture capital, and western industrial development. For entertainment there are included a rodeo and a "49-er" parade.

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ASSESSMENT WORK

Owners of unpatented mining claims should not neglect to file or cause to be filed before 12 o'clock noon of July 1 in the office where the location notice is recorded, a notice of their desire to hold their mining claims under the act of Congress signed May 3, 1943, which suspends annual assessment work on mining claims for the duration of the war.

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ACTIVITIES IN NON-METALS, MALHEUR COUNTY, OREGON

L. H. Snodgrass has a sand and gravel plant, using conventional dragline and screening equipment, located about one mile north of Nyssa in gravels bordering the Snake River.

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Mr. Chester Lackey, Ontario, is operating a sand and gravel plant on the highway just north of the Ontario city limits. Equipment includes draglines, screens, bulldozer, trucks, trencher, etc.

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Strasbaugh Sand and Gravel Company is treating and producing sand and gravel from a large deposit near the Snake River about 1½ miles north of Nyssa. Equipment includes sand pump, power plant, and screens.

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The Hardesty Division of Armco Drainage and Metal Products Co., Inc., Denver, Colorado, is making concrete pipe, including sewer, irrigation, and both plain and reinforced culverts up to 27 inches in diameter at a new plant at Nyssa. Aggregate is being obtained from Strasbaugh Sand and Gravel Company. At Ontario the Armco Company is operating a similar plant and making pipe of the following sizes: sewer, 4 inches to 24 inches; irrigation, 4 inches to 18 inches; and plain and reinforced culverts up to 54 inches.

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Oregon Clay Products Co., Inc., Vale, is installing a modern brick plant on U.S. Highway 28 near the Union Pacific Railroad at Vale.

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MISCELLANEOUS PUBLICATIONS

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