

## A CONTINUOUS X-RAY INVESTIGATION USING AN AUTOCLAVE OF THE CONVERSION OF GYPSUM TO HEMIHYDRATE

JOHN B. DROSTE\* AND RALPH E. GRIM, *University of Illinois, Urbana, Illinois.*

### ABSTRACT

An autoclave fitting into an  $x$ -ray spectrometer diffraction unit permitting continuous  $x$ -ray diffraction studies at moderately elevated temperatures and steam pressures is described. The instrument is used for the study of the conversion of gypsum to hemihydrate. Temperature and steam pressure conditions necessary and favorable for the conversion are given, and it is suggested that there is no intermediate step in the transition.

### INTRODUCTION

For years mineralogists have been interested in the range of stability of many minerals and a vast literature exists describing the stability range and new phase formation on heating for many crystalline and amorphous compounds. Until recently all the available data were obtained on samples that had been cooled to ordinary temperature and atmospheric pressure following subjection to elevated temperature and pressure. It has been assumed that the phases identified are those which existed when the sample was actually at the elevated conditions. It is obviously more desirable to identify the phases present at a given temperature, pressure, and atmosphere while the material is subjected to these conditions. Recently results have been published (Rowland, Weiss and Bradley, 1956, Weiss and Rowland, 1956, and Grim and Kulbicki, 1957) of studies of the changes taking place in the clay minerals while they are being heated by means of continuous  $x$ -rays using a small furnace mounted in the  $x$ -ray spectrometer diffraction unit. The use of the spectrometer, rather than the camera, makes it possible to literally watch one phase change to another as the sample is raised in temperature or held at a given elevated temperature.

Phase changes of minerals on heating may be related to the pressure and atmosphere as well as to the temperature. To study the effect of pressure and atmosphere as well as temperature, a small autoclave was constructed that would fit into a General Electric spectrometer diffraction unit through which  $x$ -rays could be transmitted. Results are presented herein using the apparatus for the study of the dehydration of gypsum.

### DESCRIPTION OF AUTOCLAVE

The autoclave used in this study, Fig. 1, has six essential parts: heating element, the entrance and exit ports for the  $x$ -ray beam, a sample

\* Now assistant Professor of Geology, University of Indiana, Bloomington, Indiana.

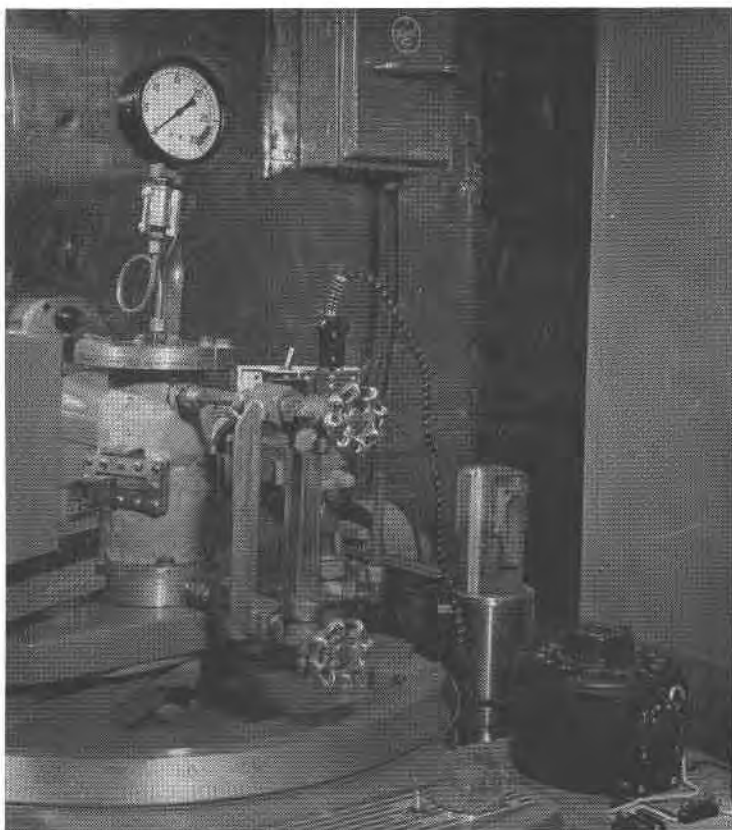


FIG. 1. Autoclave mounted in diffraction unit.

holder and sample holder stand, steam gauge, water gauge, and the container itself which consists of a stainless steel cylinder flanged at both ends to which base plates are bolted.

The autoclave has two heating elements each consisting of 12 feet of chromel (A) wire of 18 gauge wrapped around the stainless steel cylinder which is 3 inches in outside diameter with a wall thickness of  $\frac{3}{8}$  inch. One coil of wire is placed below and one above the windows. A toggle switch is included in the system which makes possible the use of one or both heating elements at once. After water is placed in the cylinder, both elements were used to raise the temperature to 100° C. After all the air is evacuated and a few pounds of steam pressure is generated, only the lower element is used so that the upper element will not superheat the steam. Current is fed to the heating elements through a variable transformer.

The windows of the autoclave are 1/16 inch sheets of beryllium which are secured to the cylinder by a double gasket arrangement. The 1/16 inch window allows a wide margin of safety for operations up to 25 pounds steam pressure. The pressure necessary to cause failure of the windows is not known, but it is above 30 pounds of air pressure at room temperature.

The sample stand and sample holder used are shown in Fig. 2. With the vertical sample arrangement used in the General Electric x-ray diffraction equipment, the sample holder presents a design problem. Since steam must completely saturate the sample, the cavity holding the sample is open at the top for the full length of the holder. Several lines of holes were drilled from the back of the sample holder into the sample cavity on a slight angle (about  $10^\circ$ ) so that the powder saturated with steam will not seep out of the sample cavity. A 1/10,000 inch sheet of mylar plastic is secured to the front of the sample holder after the



FIG. 2. Sample stand and sample holder for autoclave unit.

sample has been loaded to prevent the powder from falling out of the sample holder during the run.

The use of the steam gauge is self evident and the temperature within the autoclave is determined by consulting steam tables. A thermocouple may be inserted in the autoclave and attached to the sample, if it appears desirable. The water valve is not only very convenient, but a necessary safety device.

#### EXPERIMENTAL RESULTS

In this study gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) is treated in the autoclave with sufficient temperature and steam pressure to change it to the hemihydrate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ), and the transformation is observed by watching continuously the (020) peak for gypsum and for hemihydrate. As the water begins to leave the gypsum structure the (020) of gypsum decreases and an (020) of hemihydrate appears. By varying the steam pressure the rate of transformation of gypsum to hemihydrate can be changed. The gypsum used was from Southard, Oklahoma, and was finer than 100 mesh.

Four runs are described herein to demonstrate the kind of data obtained using the apparatus. These data are from a few of the many such runs and are typical for the gypsum-hemihydrate transformation. The per cent of the maximum (020) reflection intensity is plotted vertically and time in minutes is plotted horizontally in Figs. 3, 4, 5, and 6.

Figure 3 shows the change during a slow run. The steam pressure was elevated very slowly so that 14 pounds pressure ( $120^\circ \text{C}.$ ) was reached in 30 minutes and 20 pounds was reached 18 minutes later. The pressure was maintained at 20 pounds ( $126^\circ \text{C}.$ ) for the remainder of the run. The hemihydrate appeared when 14 pounds pressure was reached and the gypsum simultaneously began to disappear. The (020) of hemihydrate reached maximum intensity 18 minutes after it first appeared and just after the 20 pounds pressure was reached. The (020) of gypsum did not completely disappear until 7 minutes after the (020) of the hemihydrate reached its maximum intensity.

Figure 4 shows the results when the steam pressure is elevated rapidly to a high level. In 17 minutes steam pressure was raised to 23 pounds and 5 minutes later it was 25 pounds ( $130.4^\circ \text{C}.$ ). A very sharp drop of gypsum (020) intensity is accompanied by a very sharp increase (almost straight line in both cases) of the hemihydrate (020) indicating that the transformation is very rapid. In 12 minutes after the reaction started all the gypsum was converted to hemihydrate. The (020) of gypsum did not begin decreasing and the (020) of hemihydrate did not appear until 23 pounds of steam pressure was obtained. Apparently the heating rate was

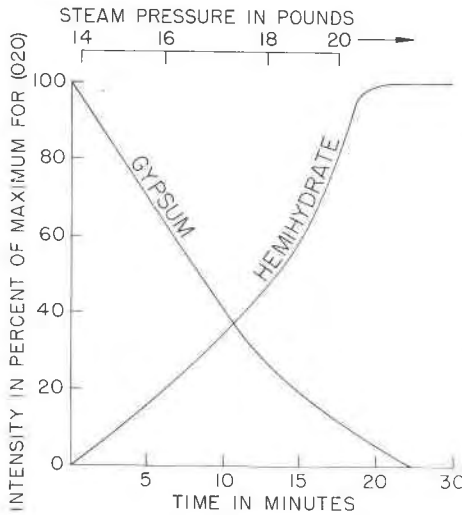


FIG. 3. Gypsum-hemihydrate transition during slow increase of temperature and steam pressure.

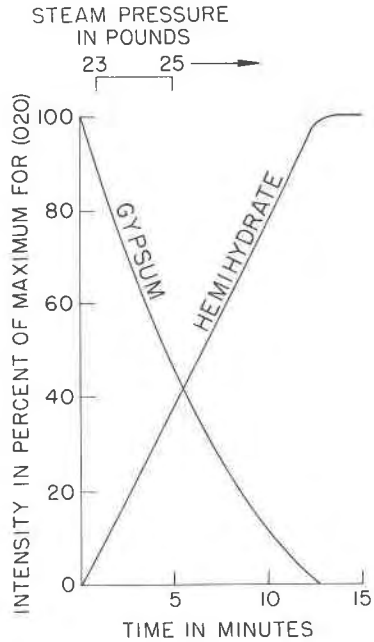


FIG. 4. Gypsum-hemihydrate transition during rapid increase in steam pressure.

so rapid that the gypsum remained even though for a time it was unstable in the environment.

Figure 5 shows a reaction similar in part to that shown in Fig. 3 in that steam pressure was never over 20 pounds. This run also has features of the run shown in Fig. 4 in that steam pressure was built up very rapidly so that 13 pounds was reached in 12 minutes, and 20 pounds 8 minutes later. The gypsum disappears and the hemihydrate appears very rapidly under these conditions.

Figure 6 shows the results of a run in which the pressure was elevated slowly at the start, and held at only 20 pounds for one hour. Under these conditions the (020) of the hemihydrate appeared 10 minutes after 15 pounds of steam pressure was reached and showed a very small gradual increase during the next 50 minutes. After one hour at 15 pounds, the pressure was rapidly raised to 20 pounds. The sample was continuously x-rayed for one hour at 20 pounds pressure and the intensity of (020) of hemihydrate showed only a very small increase. Similarly throughout the

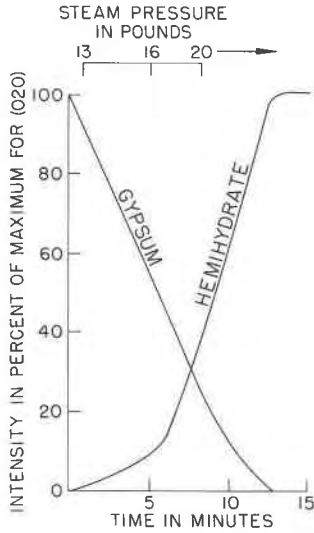


FIG. 5. Gypsum-hemihydrate transition during rapid increase in steam pressure to 20 pounds gauge.

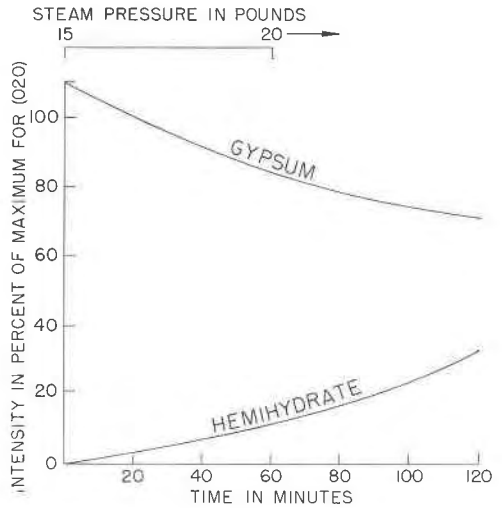


FIG. 6. Gypsum-hemihydrate transition during slow increase in steam pressure to 20 pounds gauge.

run there was only a small gradual and partial loss of the intensity of the gypsum reflection. The data suggests that complete conversion is favored by a rapid increase in pressure to something in excess of 15 pounds. Further if the pressure is initially held at a low value, later raising it to a high value does not attain the rapid conversion rate that develops with a rapid increase in pressure directly to the higher values.

#### DISCUSSION AND CONCLUSIONS

The dehydration of gypsum to hemihydrate can be "watched" continuously by the use of an autoclave built to fit in an *x*-ray spectrometer diffraction unit. The phase changes of any similar material could be followed in the same way.

The gypsum changes directly to the hemihydrate. There is no evidence of an intermediate phase. Also there is no evidence of any intermediate liquid step, even a momentary one, in the transition. In fact the data strongly suggest that such a liquid step is not present and that the transition is a direct solid state reaction. In every case the loss of gypsum and the appearance of the hemihydrate are comparable. Further, the character of the sample in the holder before and after the run does not suggest any intermediate liquid step.

Steam pressures in excess of 15 pounds are required for rapid conversion, and at 20 pounds the conversion is very rapid. If coarser material were used, it is probable that more time would be required for the conversion. It is also possible that if the rock gypsum had undergone a different geologic history than the Southard, Oklahoma area, the factors governing its dehydration might not be the same. Thus if a rock gypsum had undergone several natural gypsum-hemihydrate-anhydrite cycles, it is entirely possible that somewhat different temperatures and pressures would be necessary to cause the change from gypsum to hemihydrate in the laboratory or in industry. Further, if the gypsum contained traces of certain impurities, the conditions of conversion would probably be somewhat different.

## REFERENCES

- ROWLAND, R. A., WEISS, E. J., AND BRADLEY, W. F. (1956) Dehydration of monoionic montmorillonites: Pub. 456, Nat. Res. Council, 85-95.
- WEISS, E. J., AND ROWLAND, R. A. (1956) Effect of heat on vermiculite and mixed-layered vermiculite-chlorite: *Am. Mineral.*, **41**, 899-914.
- GRIM, R. E., AND KULBICKI, G. (1957) Etude aux Rayons X des Reactions des Mineraux Argileux a Haute Temperature: *Bull. Soc. franc. Ceramique*, **36**, 21-27.

*Manuscript received October 27, 1958.*