Proceedings of the Iowa Academy of Science

Volume 76 | Annual Issue Article 43

1969

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Measurement of Physical and Chemical Changes Induced During Weathering of A Carbonate Rock Unit

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Abstract. Changes which occurred during weathering of the Iowa Falls Member of the Mississippian Hampton Formation at Iowa Falls, Iowa were investigated quantitatively. The physical properties measured were: a) compressve strength, b) pore sized distribution, c) porosity and d) permeability. Chemically determined calcite and dolomte contents are related to the physical changes by utilization of an extensive sample sequence. The following changes are shown to be associated with the weathering process:

1) pore space and the degree of its interconnectedness increases with weathering,
2) calcite and dolomite are leached out during weathering, and
3) the rate of removal of calcite is twice that of dolomite.

The materials of a weathered rock sequence are commonly related through differences in their quantitative descriptions as fresh and altered rocks. However, the chemical changes actually occurring during the weathering process are currently only qualitatively understood because of difficulties encountered in measuring true gains and losses in a weathered sequence. The purpose of this paper is to demonstrate that weathering and similar alteration processes which result in chemical and physical changes can be studied quantitatively. This can be accomplished by calculating gains and losses on the basis of a parent-daughter relationship between samples. The ordering of the rock sequence by use of an independent parameter permits plotting these data so calculated gains and losses are presented graphically as functions of the degree of weathering. This provides a better picture of the true nature of the processes at work. This paper demonstrates how use of a variety of data and application of a constant container volume concept, (which stresses the self consistent parent-daughter relationship of a weathering sequence), makes it possible to obtain the type of data necessary to quantitatively understand the weathering processes.

The system chosen for this study represents a gradational sequence from fresh to severely weathered carbonate rock from the

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dolomitic Iowa Falls member of the Mississippian Hampton Formation in the Kinderhook Series exposed at Iowa Falls, Iowa. The samples were labelled as follows:

1) Sample IF-24, fresh rock,
2) Sample IF-24W, intermediately weathered rock, and
3) Sample IF-W, severely weathered rock

Physical Property Changes

One of the physical properties measured was the compressive strength and the results are shown in Figure 1 as stress—strain curves. The results indicate that Sample IF-24 is strongest, Sample IF-24W intermediate in strength, and Sample IF-W is weakest. As suspected strength decreases as weathering progresses.

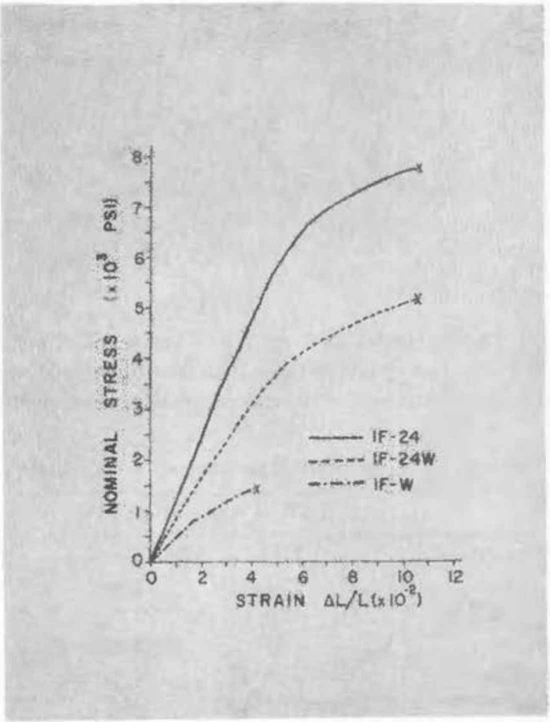

Fig. 1. Stress-strain relationships for samples.

Figure 2 shows the pore size distributions for the samples as determined by mercury injection techniques (Hiltrop and Lemish 1959). The distributions are normalized and show that weathering

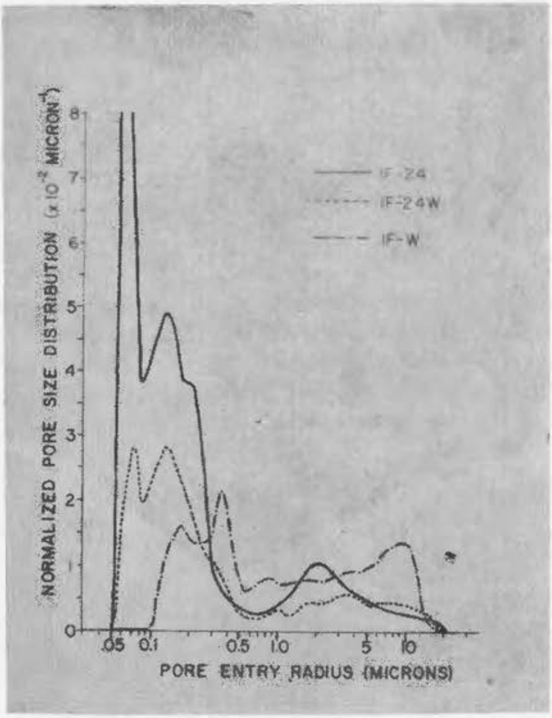

Fig. 2. Pore size distributions.

creates larger pore entry radii at the expense of smaller ones as demonstrated by the shift of the distribution maximum toward larger pores coincident with the increased degree of weathering.

Table 1. Summary of the physical properties for the sample sequence

Property	IF-24	IF-24W	IF-W
Degree of Wathering	Fresh	Intermediate	Severe
Porosity-Hg (%)	2.37	14.96	25.30
Porosity-H_2O (%)	4.76	20.08	32.15
Bulk Density (g/cc)	2.637	2.266	1.867
Rock Density (g/cc)	2.698	2.657	2.545
Permeability (darcy)	0.011	0.096	0.300
Yield Strength (psi x10^3)	6.40	3.75	0.75
Fracture Strength (psi x 10^3)	7.75	5.10	1.43

Physical properties measured are listed in Table 1. From the values obtained for each property the following consistent trends for the unweathered to weathered sequence are:

1) density is decreasing,
2) strength is decreasing,
3) porosity is increasing,
4) permeability is increasing,

and as was shown earlier,

5) the pore entry radius maxima indicate larger pores and broader pore size distributions in the weathered rock.

These observations establish the quantitative aspects of physical changes and focus attention on the problem concerning the direction of net chemical changes accomplished by the weathering process.

Chemical Property Changes

On an atomic scale the results of the weathering process are expressed as gains and losses of chemical elements between fresh and weathered rocks of a sequence. The chemical composition of these rock materials can be determined and may be reported as weight-percent data. Differences in these weight-percent data can be used to recognize the presence of a change and to infer differences between samples of a weathering sequence. This traditional approach is contrasted with the application of the proposed unit container volume concept which stresses the self consistent parent-daughter relationships of the weathering sequence.

Weight-Percent Approach

The samples were analyzed by procedures outlined by Bisque (1961), and the results are presented in Table 2. In order to

Table 2. Table of chemical analysis data for sample sequence

Weight Percent Oxide	IF-24	IF-24W	IF-W
CaO	32.06	31.40	31.48
MgO	18.26	18.67	18.96
CO_2	45.09	45.01	45.39
Insoluble Residue	0.09	0.18	0.23
Fe_2O_3	0.23	0.52	1.13
Calcite[1]	11.89	9.71	9.11
Dolomite[2]	83.51	85.37	86.70

[1]Calcite = [CaO — MgO (1.3908)] [1.7847]
[2]Dolomite = (MgO) (4.5734)

demonstrate graphically the chemical changes associated with weathering, the porosity of the samples is used as an independent parameter in Figures 3, 4, and 5. Porosity was chosen because it shows an approximate linear trend as weathering progresses. Figure

3, a plot of chemical data for the major mineral phases as reported for each sample, shows that dolomite content increases and calcite decreases with weathering expressed as increasing porosity. The slope (m) of a line connecting Samples IF-24 and IF-W is given as an aid in comparing the magnitude of change. In the reporting of weight percent data the percentages of all components present in each sample must sum to one hundred percent. This is shown in Figure 3 by the mass being one hundred for all samples since on this basis the percentage shown is numerically equal to its mass in grams. Because each sample must sum to 100, a change in any one component will influence the value reported for all other components. As a result of the above mathematical restriction there exists several ways to account for variations in the reported weight percentages for a sample sequence. In this sample sequence several equally valid interpretations for mineral changes occurring during weathering would yield the same weight percent results. Some of these interpretations are:

1) the dolomite content is increasing,
2) the calcite content is decreasing,
3) both of the above occur simultaneously,

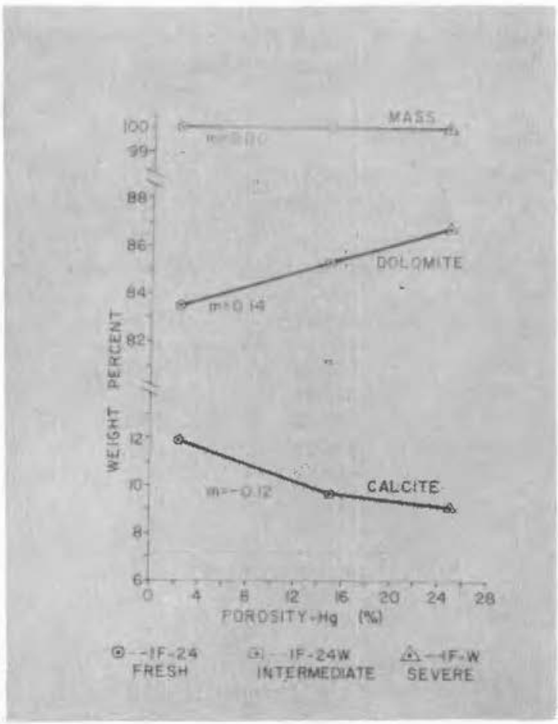

Fig. 3. Comparison by weight-percent approach.

4) both calcite and dolomite are being added, but at different rates, and
5) both calcite and dolomite are being removed, but at different rates.

Herein lies the inherent dilemma associated with the use of weight percent data for comparative purposes. Which of the above interpretations best accounts for physical changes?

Unit-Container-Volume Approach

Another approach, which gives an accurate picture, is to consider the weathering process in terms of a sample container of unit volume. This idealized volume will be constant during weathering. Materials leave or enter this container depending on the process operative. One can follow the changes on the basis of a parent-daughter relationship between materials of a sample sequence by comparing the mass present within the unit container volume of each material. Consider the fresh rock as a parent, the intermediate weathered rock as a first daughter, and the severely weathered rock as a second daughter, etc. The mass within a *unit con-*

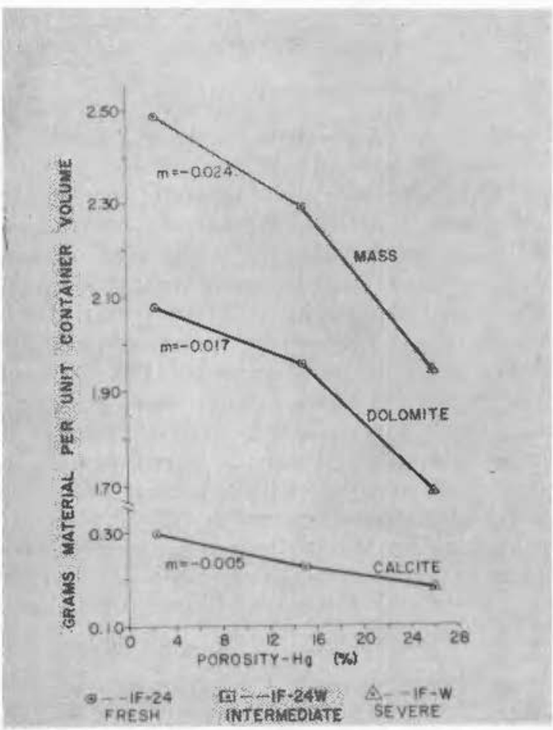

Fig. 4. Comparison by unit-container-volume approach.

tainer volume of any material may be calculated by dividing the total mass of a core sample by its volume. Mass differences should show the kinds and directions of chemical changes during weathering (Elwell, Simon, Lemish, 1968).

In Figure 4, the observed chemical changes for the two major mineral phases of the dolomitic rock are determined for a parent-daughter relationship. IF-24 is the parent, IF-24W is daughter I, IF-W is daughter II. An important aspect is the effect of mass action. The Law of Mass Action essentially states the greater the quantity of a material available for reaction, the larger the amount of material participating in the reaction. Because the rock is mostly dolomite, net gains and losses of the rock most closely reflect changes in this mineral. This is seen in Figure 4 by comparison of the slopes for dolomite and calcite with the total mass change.

Note that on a rock basis, calcite and dolomite are both progressively removed from the rock during weathering, coincident with a decrease of total mass in the unit container volume. From this observation we can immediately reject all the interpretations deduced from weight percent comparisons but the 5th, which stated that calcite and dolomite are being removed but at different relative rates.

Chemical Reactivity of the Minerals

Another advantage of the unit container volume approach is that relative rates of removal for each mineral in the container independent of mass action can be quantitatively shown. Because we are dealing with a net material balance between parent and daughter materials, relative changes in the rates of removal of a mineral may be obtained experimentally without knowledge of the degree of attainment of solution equilibria. In this case the effect of mass action is removed by using sets of samples of different sizes such that each parent material contained 100 moles of a given mineral to be studied. Then the ratio of moles of this mineral remaining in each daughter sample to the 100 moles in the parent results in plots as shown in Figure 5. The amount of calcite removed relative to the amount originally present is 40 percent. However, the amount of dolomite removed is only 20 percent. The relative rate of leaching for the calcite is two moles for each mole of dolomite removed which shows that calcite is preferentially extracted. Is this observation consistent with outcrop and petrographic observations?

Petrographic Observations

Petrographic study of the sample sequence qualitatively indicates that interstitial calcite is being progressively removed from

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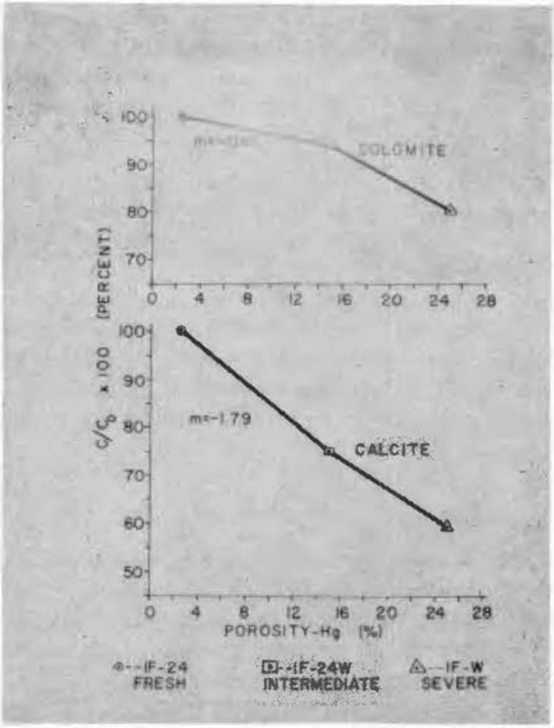

Fig. 5. Molar ratios for calcite and dolomite of parent-daughter samples.

the dolomite matrix. Visual observation at the sampling site for IF-W showed that the final weathering product is an unconsolidated dolomite sand. Mason (1961) also found this to be the case at other outcrops of this Iowa Falls member. Thus this independent qualitative information is consistent with the calculated quantitative changes.

Discussion

The physical properties measured showed changes occurring during weathering of the dolomitic rock. These changes included development of higher porosity, higher permeability, and larger pores along with a decrease in the density and strength. Petrographic evidence qualitatively indicated that interstitial calcite was progressively removed resulting in a dolomite sand. The comparison of chemical weight percent data between samples did not indicate any definitive process. Through the use of the proposed unit container volume concept it was quantitatively shown that both calcite and dolomite were removed from the rock during weathering. The quantity of dolomite removed from the rock is greater than the quantity of calcite. However, the relative rate of removal for the individual mineral phases, neglecting their abundance showed two moles of calcite removed for each mole of dolomite. This indicates that the mineral calcite is preferentially removed, even though it is less abundant in the rock.

Once it is known that both dolomite and calcite minerals are being removed from the rock the problem of naming the net operable process is made easier. If dolomitization and dedolomitization are restricted to changes in carbonate structures both of these processes may be rejected. Dolomitization is rejected because of the net loss of magnesium from the rock. Dedolomitization is also rejected because of the preferential loss of the calcite mineral. In this case the increasing relative abundance of dolomite in respect to calcite is best explained as residual enrichment, resulting from the selective removal of calcite.

Conclusions

Application of new methods and the combination of several types of measuring has permitted the determination of quantitative changes during weathering. Consideration of all data demonstrates some important conclusions regarding weathering which may be looked at from both a rock and a mineral level.

1) On the rock level, bulk changes show that most of the material removed is dolomite.
2) However, on a mineral level calcite is removed faster than dolomite, and results in a sanded dolomite.
3) Thus the dolomite is being residually concentrated even though it is the bulk of the material removed.
4) The relationship of these chemical and physical changes indicate the manner and rate at which material is removed from the rock during weathering. The removal of material explains the observed decreasing density and strength and the increasing porosity, permeability, and pore entry radii.
5) Although standard chemical and petrographic methods qualitatively show that weathering increases the relative abundance of dolomite, it is only the proposed unit container volume method that permits quantitative detection of the process responsible for net chemical and physical changes.
6) The unit container volume method provides a basis for a material balance so that the analytical results may be related between samples as gains and loses of materials. This problem is an old one. Krauskopf and others have rec-

ognized all that is necessary to solve the dilemma of weight percent data is "to have independent evidence as to how the mass or volume of the rock has changed during weathering" (Krauskopf, 1967). Our method now provides this evidence.

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