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POTENTIAL BY-PRODUCT ELEMENTS IN THE PHOSPHORIA FORMATION OF THE WESTERN STATES

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by V. E. McKelvey

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Phosphate rocks have long been known to contain other elements and compounds besides lime and phosphate, but in recent years the list of elements reported by various investigators from phosphate rocks over the world has been extended to include well over half of all of the known elements. In addition to elements required by the chemical structure of phosphate minerals, the list now includes antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, chlorine, chromium, cobalt, copper, fluorine, gallium, gold, indium, iodine, iron, lead, lithium, manganese, molybdenum, nickel, palladium, platinum, rare earths, radium, rubidium, selenium, silver, strontium, sulphur, tantalum, thallium, thorium, tin, titanium, tungsten, uranium, vanadium, zinc, and zirconium.

Many of these elements are of interest because they are essential, if only in small quantities, to plant growth. Others are of concern because they must be removed from the phosphate rock before some of the chemical products manufactured from it can be utilized without deleterious effects. A few are perhaps of more direct economic interest because they occur in such form or quantity as to suggest

that they might be recovered as a by-product of the mining or processing of the phosphate rock. Like the phosphate itself, however, these potential by-product elements can be freed only by complex and costly chemical methods. Even so, methods have been found to recover some of them and it is possible that technological advances may make possible the recovery of others.

Because of the potential importance of these elements, both, to industry and the National economy, the Geological Survey has paid particular attention to them in its studies of the Permian Phosphoria formation of the western states. In this discussion of the potential by-products in the Phosphoria formation, I wish to make clear, however, that we do not claim that all of them can be recovered economically by known or established methods. Although the search for such elements is properly one of our functions, I believe that the research on methods for their recovery must be done largely by industry.

Not all the elements previously mentioned are present in the Phosphoria formation but of those present, at least eight occur in sufficient amounts to warrant further study as potential by-products. These elements include fluorine, uranium, rare earths, vanadium, silver, nickel, zinc, and molybdenum. Of these, fluorine, uranium, and rare earths are most concentrated in the phosphate rock and probably occur in the phosphate mineral. Vanadium and silver are found in significant quantities both in the phosphate rocks and in the weakly phosphatic shales and mudstones associated with them. Both may occur in the phos-

phate mineral but the most significant quantities probably occur in clay minerals. Although zinc, nickel, and molybdenum are trace constituents of the phosphate rocks, their highest concentrations are found in some of the more weakly phosphatic mudstones and shales. It is probable that they, like some of the silver and most of the vanadium, are tied up in clay minerals.

Fluorine is of course an integral part of fluorapatite, which makes up the bulk of western as well as other domestic phosphate rocks. Few phosphate rocks contain less than about one-eleventh as much fluorine as phosphate; most of the western rocks contain a tenth or a ninth as much fluorine as phosphate and some contain as much as an eighth. In other words, the fluorine content of a rock containing 32 percent P_2O_5 may range from about 2.9 to over 4 percent. Although most of the fluorine is present in fluorapatite, small quantities of free, purple fluorite are found in some of the rocks which have a high fluorine-phosphate ratio. Although some of these fluorite-bearing rocks have been found to contain over 8 percent fluorine, the fluorite is secondary and does not persist laterally in such high concentrations. Our observations to date suggest that the fluorine-phosphate ratio in most of the phosphate rocks decreases from east to west, although the total amount of fluorine in the whole formation increases in the opposite direction with the westward thickening of the phosphatic rocks.

in the phosphate mineral and it seems probable that it substitutes for calcium in the fluorapatite lattice. Uranium, like the other minor constituents, would probably have value only as a possible by-product.

Rare earths of the cerium group were first discovered in apatites and phosphate rocks by a Russian about 25 years ago in amounts as high as 0.3 percent in the bedded phosphorites and 3 percent in the Khibinian apatites. Other Russian investigators have shown recently that the rare earths of the apatites can be recovered in the acidulation of phosphate rock with hydrochloric acid. Recent analyses made by W. O. Robinson of the Bureau of Plant Industry on three western phosphate rocks show them to contain about five to fifteen hundredths of a percent of rare earth oxides and one analysis of our own shows the same order of magnitude. Additional analyses may disclose higher concentrations but until more analyses are made, and until the identity of the rare earths is known their potential value is difficult to establish. At present prices the rare earths contained in the western rocks might be worth $0.50 to $1.50 a ton.

Vanadium has been known in western phosphate rocks since 1911, when it was discovered by chemists of the U. S. Geological Survey. Although the vanadium is not a part of the phosphate mineral nearly all western phosphate rocks contain it in amounts

In 1928 Jacobs and his colleagues in the Bureau of Plant Industry first emphasized the large reserves of fluorine contained by our domestic phosphate rocks and since then the problem of fluorine recovery has received considerable attention. Some fluorine is recovered now as silicofluorides but the recovery of fluorine as such, or as calcium fluoride has thus far proved too costly. Within the last year, however, TVA has demonstrated a method for the recovery of fluorine in a dry limestone-packed tower during the manufacture of fused tricalcium phosphate and a patent has been taken out for the defluorination of phosphate rock by injection of limestone into stack gas. Inasmuch as the total amount of fluorine contained in the phosphate currently mined domestically is nearly twice that mined as fluorspar and as our fluorspar reserves are limited, it seems apparent that the problem of fluorine recovery is one of National importance.

Although uranium was discovered by the French in Algerian phosphates in 1924, and by the Russians in some of their deposits in the early thirties, it was not discovered in the Phosphoria formation until 1944, when, of course, we had good reason to look for it. Since then, we have made rather extensive studies of its occurrence and distribution over the entire field. The uranium content of the western phosphate rock in common with the uranium content of other phosphorites and some black or bituminous shales is generally measured in thousandths of a percent. For the most part, the uranium is in the high-grade phosphate rock. Several lines of evidence suggest that the uranium is

ranging from 0.1 to 0.3 percent V_2O_5; in fact, concentrations of as high as 0.5 percent V_2O_5 are found in places. Since 1941 the Anaconda Copper Mining Company has been recovering vanadium as a by-product of their phosphoric acid manufacture. At present prices the value of the vanadium in the high-grade phosphate rock ranges from about $1.00 to $3.00 a ton.

Just before the war W. W. Rubey of the Geological Survey found that the highest concentrations of vanadium in the Phosphoria formation occur in shales and mudstones that are only weakly phosphatic. One zone in particular near the upper phosphate zone was found to be especially vanadiferous. In the course of studies carried on during the war by the Geological Survey, the Metals Reserve Company and the Bureau of Mines, this zone, which we call the vanadiferous zone, was found to average about 3 feet in thickness and to contain about 0.75 percent V_2O_5 in several large areas in western Wyoming. In the Paris-Bloomington area of southeastern Idaho, the same zone averages over 10 feet in thickness and contains nearly 1 percent V_2O_5. Although plans for the development of these deposits were curtailed when the vanadium shortage was alleviated by increased production of ore from other areas, metallurgical research had progressed far enough to suggest strongly that vanadium could be produced from them if not at a profit, at least at no great loss. Although they may not be exploited for some time to come, there is little doubt that these deposits constitute our largest reserves of vanadium.

Silver was first discovered in the vanadiferous zone of the Phosphoria formation in 1944 by the U. S. Bureau of Mines and since then it has been found to be a common trace constituent in the phosphate rocks not only in the Phosphoria formation but over most of the world. In fact, trace amounts of silver have been found in about 85 percent of the several hundred samples spectrographically analyzed for us by the Bureau of Mines. Concentrations of about an ounce per ton have been reported by spectrographic analyses but the maximum concentration found in the few samples thus far analyzed chemically is only about a quarter of an ounce per ton. If the maximum concentration proves to be of the order of magnitude now indicated by the chemical analyses it is unlikely that any could be recovered economically.

Although zinc, nickel, and molybdenum are trace constituents of the phosphate rocks their highest concentrations generally are found with vanadium in the weakly phosphatic mudstones and shales. Enough samples have not yet been analyzed to establish the persistence of these elements but concentrations of about 1.3 percent zinc and 0.1 percent molybdenum have been found in the vanadiferous zone of southeastern Idaho and western Wyoming. The highest concentrations of nickel--about 0.3 percent--have been found in another shale bed stratigraphically below the vanadiferous zone. Because the beds containing these elements are weakly phosphatic, it is improbable that they could be produced as a by-

product of the processing of phosphate rocks, but it is possible that they could be by-products of the mining, either open-cut or underground, of phosphate rock.

Two other substances--oil and sulphur--may be mentioned as having possible economic significance in the Phosphoria formation. As much as 25-30 gallons per ton of distillable hydrocarbons have been found in the phosphatic shales in the vicinity of Dillon, Montana, but elsewhere in the western field the concentrations are much lower. Most of the rocks of the Phosphoria formation are rich in organic matter, however, and it is possible that thermal methods of processing the rocks may utilize this heat value to some extent.

Many of the phosphate rocks contain two or three percent total sulphur as SO_3. The highest concentrations, however, are found in the associated shales and mudstones, a few of which contain as much as 10 or 12 percent of total sulphur as SO_3. Although the sulphur occurs in several forms, most of it in the weathered rocks is present probably as sulphates and most of that in the fresh rocks is present probably as sulphides. Though it seems unlikely that any of this sulphur can be recovered or utilized in any of the various methods of processing, it is worthwhile to keep its presence in mind.

Though further work may not much extend the range of concentration of the elements already discussed or lead to the discovery of other elements, we intend to keep looking. The search is a costly one, however, because prospecting cannot be done by the usual methods.

None of the elements already discussed, except fluorine, can be detected visually or even microscopically in any of the rocks, even those in which their concentration is greatest; prospecting, therefore, must be carried out wholly in the laboratory. Although spectrographic methods can be and are being used as an inexpensive method of analysis, the spectrographic sensitivity of many of the elements is so low as to prevent their detection by the usual spectrographic methods. Moreover, the procedures for the chemical analysis of some of these minor elements in phosphate rock are either not reliable or are time-consuming and costly.

In summary, we do not expect that all of the elements or substances discussed here will be recovered, either singly or collectively, in the course of mining or processing the phosphate rock by any or all of the various methods now in use. But as each of the elements discussed could add $0.50 to $2.00 a ton to the value of the rock we feel that further research on methods for their recovery is amply justified by economic considerations alone. Eventually, of course, we may have to consider recovery of some of these elements, such as fluorine, for reasons of mineral conservation and we may then have to consider them, not as by-products, but, to use a term of T. S. Lovering's, as co-products, each of which is as important as the other.

In this connection it is interesting to note that something approaching this philosophy is now being followed in the Swedish

black shale industry. In 1947 Dr. Josef Ecklund of the Swedish Geological Survey told me that the Alum shale of Sweden now yields 5 percent of the rock by weight as oil; an additional 3 percent in oil equivalent is converted into steam and thence into electric power; the rock contains 5 percent of sulphur but they only recover 2 percent; in so doing, however, they supply 25 percent of Sweden's national sulphur requirements. The rock is finally blown into rock wool and somewhere along the line 0.4 percent V_2O_5 is recovered from it. Presumably they are also recovering uranium from these rocks, though I don't know at what stage. Only in case a nation is in short supply is it likely to display such resourcefulness and ingenuity and we hope that if such practices develop in our phosphate industry they will be brought about by the promise of profits rather than by the threat of mineral shortages.