

# The Metallurgy of the Rarer Metals\*

Whose Cheap Production Offers an Attractive Field for Research

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THERE are many metals which may be called "the rarer metals." Among them the most interesting by far, to the metallurgist and to the economist, are those metals whose compounds are relatively cheap but which command a high price because of the difficulty of their reduction. These are the metals whose market price may at some time be reduced one half, three quarters, perhaps nine-tenths, by improved methods of reduction, and the discussion of how this might be accomplished and to what uses these metals at such low prices might be put, is interesting to the border of fascination.

If this article were being written thirty years ago, aluminium would be one of the metals to be discussed. It is now out of that class, but in 1886 it was one of the rarer metals, selling at \$10 per pound, although its ores were "as common as dirt." At that time you could buy a ton of bauxite ore containing 6/10 ton of alumina or 3/10 ton of aluminium for \$5, while the 3/10 ton of aluminium was being sold for \$3,000, at wholesale. Or, eliminating the purely chemical work, 6/10 ton of chemically purified alumina could then have been bought for \$50, while the aluminium it contained was worth on the market sixty times that amount. Such were the metallurgical conditions in the aluminium industry thirty years ago, and so attractive were they to experimenters and inventors that the genius of the profession expended its best talents on the problem, with the result, in less than ten years, of reducing the market price to less than one tenth its former figure.

The silicon industry furnishes another example in point. Silica is the most abundant and cheapest material in nature, yet silicon was selling in 1900 as a chemical curiosity at over \$100 an ounce. Imagine the stirring up which my metallurgical wits received, when in 1902, Mr. Tone, at Niagara Falls, showed me a barrel full, 100 pounds perhaps, of silicon made in his electric furnace, and asked me what uses it could be put to. At the present time, 10 cents per pound is a good market price for silicon, which is often sold by the carload.

It is such seeming fairy tales as these which constitute the fascination of those metals which are abundant in nature but whose high cost rests on the difficult and costly methods of reduction employed. Such opportunities exist, for our rising generation of chemists and metallurgists to make themselves famous and, incidentally, rich—but they will find their fame more of a reward than their riches.

Among the metals at present of high price, but which by improved metallurgical processes might be made very cheaply, are beryllium, boron, magnesium, calcium, strontium, zirconium, molybdenum, barium, titanium, chromium and cerium (mixed metals of the cerium group).

## BERYLLIUM.

Commencing with one of the light, alkaline-earth metals, its ore is not as rare as is ordinarily supposed. Most non-mineralogists link it with beryl, and think of the latter as a very pretty and very expensive gem—the emerald. But the emerald is only the clear green or aquamarine stone, while massive beryl, looking like massive green quartz, is much more common, and is even abundant in some localities. The beryl crystals of Acworth, N. H., are sometimes as large as a barrel, and the massive beryl at this locality is quarried like feldspar. Its composition is

SiO <sub>2</sub> .....	67.0 per cent
Al <sub>2</sub> O <sub>3</sub> .....	19.0 per cent
BeO .....	14.0 per cent

It is difficult to say what the price of this material would be if it was desired by the ton, but it should not be expensive. When chemically treated, both the Al<sub>2</sub>O<sub>3</sub> and the BeO which it contains could be separately obtained.

Up to the present, no one has succeeded in isolating the metal except by reducing a halide salt of beryllium by potassium or sodium (Bussy, Wöhler, Debray, Menier, Reynolds, Nilson and Petterson, Kruss and Moraht) or by electrolysis of double chloride, bromide, or fluoride of beryllium and sodium or ammonium (Borchers, Warren, Lebeau, Liebmann).

These methods are tedious and costly for two reasons: First, they require the conversion of the beryllium

into an anhydrous halide salt, which is a difficult chemical operation, and, second, the electrolysis sets free the halogen, which is very destructive of electrodes and apparatus. It is not to be expected that beryllium can be made cheaply until someone masters the direct electrolysis of the oxide, dissolved or suspended in a more stable melted salt. This is by no means an impossibility; a similar solution was found for the aluminium problem, and systematic, determined search would in all probability find the answer for beryllium. In such a case, the cost of the metal would depend only on the cost of beryllium oxide, being probably not more than 20 cents per pound plus the cost of the oxide. Since BeO is only 36 per cent Be, it would require 3 pounds of oxide to give one of metal; if the oxide cost 10 cents per pound, the total cost of the metal should not exceed 50 cents, by such a supposition process. Dealers in rare chemicals will charge you, at present, \$300 per ounce for a specimen of it.

Lebeau has produced beryllium bronzes by reducing directly, in the electric furnace, a mixture of beryllium oxide, copper oxide and carbon; 0.5 per cent of beryllium makes copper hard and sonorous; 1.5 per cent makes it yellow, and 5 per cent makes a fine golden yellow bronze.

Beryllium, like any other rare metal, must find uses which justify its cost. Being white, malleable and unchanged in air, its specific gravity, 1.64, would make it particularly useful for objects where great lightness and permanence in air is the first consideration and cost secondary. So far we practically know nothing about its tensile strength or rigidity, about how it might be strengthened or stiffened by small additions of magnesium, or aluminium or even of zinc, or copper, or manganese, or some other metal. We do not yet know the mechanical properties of its fine bronzes, except that they are somewhat similar to aluminium bronze, but in what respects they might be superior or perhaps unique is unknown. Finally, the metal may easily possess special properties, now unknown, which may render it particularly useful for some specific purpose. Its specific heat, for instance, is the highest of any useful metal, and its latent heat of fusion must be abnormally high, possibly 300 calories, and its latent heat of vaporization probably higher than that of any known element except carbon or boron. Such characteristics might give it special uses in electrical instruments or for physical apparatus, where its cost would not exclude its use. Altogether, beryllium is a metal which will well repay extended metallurgical research and minute physical and chemical study of its many unique properties.

## MAGNESIUM.

The metallurgist has been coquetting with magnesium for half a century, and has, as yet, not made a fraction of the progress which he should have made. We can get its oxide cheaply and in abundance, its salts are not very difficult to prepare, we know their properties to a considerable extent, we know almost all the properties of the metal which bear on its isolation, and yet the industry lags and halts as if there were no such thing as modern metallurgy. To prepare by tedious methods the anhydrous double chloride, and then to electrolyze it about as Matthiesen did fifty years ago, is nearly all that can be said with certainty about its present metallurgy. At any rate, using magnesium oxide costing a few cents per pound, the metal sells for about as many dollars per pound, and yet there is a great scarcity of the metal.

Dr. W. M. Grosvenor, in a recent paper before the American Electrochemical Society, summarizes the present methods of production and the uses of the metal. Happily he also suggests the great field open for improvement, especially for radically new metallurgical methods of production. With magnesium in its salts costing less than 8 cents per pound, he places the actual cost of the metal at \$1 per pound, leaving over 90 cents per pound for the cost of its extraction. "Brethren, these things ought not so to be." Speaking with the enthusiasm born of past achievements in electrometallurgy, along entirely analogous lines, a modern, up-to-date attack on this problem ought to result in producing magnesium at 25 cents per pound.

The point of attack should be undoubtedly to reduce the oxide directly. The halogen salts are hygroscopic, and the halogen is destructive of the reducing apparatus. It is almost certain that proper research will

enable the electrometallurgist to feed MgO directly into an electrolytic bath of fused salts and take magnesium or magnesium alloy from it. The pure metal will float on almost any fused salt, but its alloy with heavier metals may be made such as to sink, and many of its alloys have immediate useful applications.

Dr. Grosvenor makes suggestive remarks about the reduction of magnesia by carbon. If the boiling point is only 1,200 deg. Cent., then a process of reduction similar to that of zinc oxide might be practicable if we could (1) find a retort material which will stand the temperature required (1,800 deg. to 2,000 deg. Cent.), and (2) condense the vapors without contact with air. Fortunately, magnesium does not form carbide at high temperatures, so that its reduction is simpler by that much. Dr. Grosvenor speaks of a chemical process which will use cheap raw material, a moderate amount of fuel, and give a fair efficiency of reduction. With all expenses added, he estimates a cost not over 35 cents per pound. This may be true, but whether it materializes or not, he and his colleagues have the right vision of the possibilities, I may even call them the probabilities, of this field; they are truly "absolutely fascinating."

While the world-war lasts, with its enormous demand for magnesium for military purposes, the price will remain in the dollars per pound. But experience in this line is being rapidly accumulated, and improvements are undoubtedly rapidly succeeding each other, although keen competition is keeping them secret as far as possible. After the war's close, with normal industrial conditions reappearing, magnesium will undoubtedly sell at a price which will take it out of the class of the rarer metals and put it among the common ones. As the price goes down its industrial uses will increase in a geometric proportion, and instead of production being expressed in thousands of pounds per year it will reach thousands of tons. This will be another of the by-products of the great war's stimulus to metallurgical industry.

The possibilities held out to the metal industry by reasonably cheap magnesium are extremely interesting. The stiffening of magnesium to produce strong alloys with specific gravity not over 2 has not been properly studied. It is quite possible that alloys analogous to *duralumin* may be discovered, as strong as soft steel and only 30 per cent of its weight, which will find extensive use in aeroplanes and dirigibles. Such alloys may also largely displace aluminium alloys, which are used by thousands of tons annually in the automobile industry, with a saving of one-third in weight, which will compensate for a higher first cost. The metallurgical uses of magnesium will also be greatly extended by its lower price, such as for deoxidizing brass, bronze, nickel, monel metal, since it is a much stronger deoxidizer than aluminium. In fact, aluminium has blazed the way into numerous uses for which magnesium, as soon as it becomes cheaper, will compete and replace its older sister. With supplies of magnesium ore as plentiful as those of aluminium ore, and the metallurgist awake to his responsibilities and producing the metal cheaply, there will inevitably be a large future for magnesium as one of the common metals of everyday life.

## CALCIUM, STRONTIUM, BARIUM.

These are a trio of highly interesting elements, common enough in nature, but all scarce and of high price because of the metallurgist's lack of efficient and cheap methods of reduction. With burnt lime, CaO, one of the cheapest of common materials, strontium sulphate, a mineral found in considerable abundance, and barium sulphate, so common, as heavy-spar, that it is used as an adulterant for some cheap paints, the metallurgist is again faced with the demand for cheap methods of reduction. And yet, although calcium is sold at a few dollars a pound, strontium and barium cost several dollars per ounce. Here is a two-fold need: first, cheap production; second, a thorough study of these metals to find out their specific properties and their particular uses. Which should be undertaken first is an interesting topic for discussion. Historically, the metallurgist has usually produced the metal first and then studied its properties and possibilities; at present, with these metals already at hand, metallurgical activity might be greatly stimulated by extensive studies of the properties, alloys, and chemical uses of these elements. Our present information in this direction is fragmentary

\*A paper read at the Cleveland meeting of the American Institute of Chemical Engineers on June 14, 1916.

and partly unreliable as far as it goes. A Carnegie Research scholar, or even the Bureau of Standards, by disclosing to us some of the unknown properties of these elements, might stimulate the experimenter to renewed efforts to find cheaper methods of reduction.

**Calcium**, at the present time, is the best known of these three elements. The method of electrolyzing its fused chloride and lifting the metal away from the surface, as an irregular stick, has been fairly successful, and since the chloride is not difficult to dehydrate, the whole operation is not very expensive. Calcium is therefore, at present, perhaps a semi-rare metal, which could be produced much cheaper even by present methods if made on a large scale to fill a large demand. The method of production is easily susceptible of minor improvements, and the chlorine is a valuable by-product to the manufacture. The principal hitch at present is in finding the uses for a large production of calcium. Here is where extensive study of the properties and possible uses of calcium would greatly stimulate the metallurgical industry. With specific gravity of 1.85, its possible alloys with other light metals should be exhaustively studied; quite possibly some of them are strong, resistant to air and water, perhaps even to acids. Calcium tarnishes easily in the air, and magnesium also, but it is quite possible that some alloy of the two does not tarnish, and may have valuable mechanical properties. Another large possible use is as a chemical purifying agent in melting and casting metals. Calcium-silicon-aluminum alloy has already found application as a deoxidizing agent in steel, because while aluminum oxide and silicon and their combination with each other are infusible at steel-melting temperature, and therefore are eliminated slowly from the metal, calcium oxide forms with these an easily fusible slag, which easily rises out of the molten metal. It is quite possible that a small addition of metallic calcium may in a similar manner reduce the amount of sulphur and phosphorus in steel, because it is either as calcium sulphide or calcium phosphate that these elements are eliminated in refining steel. Other metals and alloys whose properties are damaged by sulphur or phosphorus may be similarly refined or improved. The alloys of calcium with copper, tin, bronze, brass, monel metal, and other commercial alloys have not been studied; until they are, no one knows how many useful mixtures may exist with particular properties of industrial value. The question of adding calcium to the light stiff aluminum alloys, for instance, is worthy of attention, but has not been touched.

**Strontium** is a silvery-white, very soft metal, with properties similar to calcium, density 2.54. Its ores cannot be called rare minerals, and it is a rare metal, therefore, only because of the difficulty of its isolation. It is chemically very active, and electrochemically extremely hard to manage. It has about the same specific gravity as its fused salts, so that it neither rises nor sinks in any of them quickly; it seems also to redissolve in its melted salts with great velocity, so that very high current density is required to obtain any metal at all. Its surface tension appears to be abnormally high, so that it separates out in more or less minute globules which are highly indisposed to running together into one mass. What an attractive subject this forms to the electro-chemist who really wants to meet difficulties and taste the joys of overcoming them. And then one may well ask: To what purpose? Here, again, we do not know, but we can feel confident that in the innumerable list of possible combinations of metals strontium might have properties different from any other element, which would lead to its employment on a large scale. These are all questions of the future which form the undiscovered country open to the investigator and chemical pioneer. We may well thank our stars that the world of science still holds unexplored areas to tempt the adventurous investigator and to reward the *Wanderlust* of the metallurgical pioneer.

**Barium** is common in its compounds and almost unknown in itself. Under electrolytic conditions where calcium comes out *en masse*, and strontium separates as small globules, barium is obtained only as a fine powder. Its density is 3.75, but its salts are heavier than the corresponding strontium and calcium salts, so that the fine powder may sink or swim, largely according to the temperature. And yet the fused barium salts are very lecent and manageable salts, easily obtained anhydrous and melting cleanly. Their electrolysis, however, is nearly the most difficult task that the electrometallurgist can take up. But it should be taken up and mastered, because a metal so common in its compounds could be obtained in large quantities if uses for it were developed, and if our modern electrometallurgists are worthy successors of Faraday, Bunsen and Castner, they should vigorously attack the problem of its cheap extraction. Even if their end was not reached, they would be whetting their metallurgical wits upon the finest of chemical

whetstones, and their experiences would be of value to themselves as well as to other lines of electrometallurgy.

#### BORON.

As an intermediate element, semi-metal, cheap and abundant in its compounds yet almost unknown as an element, boron is very interesting. Although quoted at several dollars an ounce, yet there are possibilities of it being made for  $x$  cents per pound, where  $x$  may be anything over 25. It is only the prophetic prescience of the enthusiastic metallurgist, however, that can discern this goal in the distant future.

Boron occurs in nature as its oxide, sassolite, containing 31 per cent of boron; as borax, containing 11.5 per cent of boron, and as colemanite, containing 18.9 per cent of the metal. These sources are comparatively abundant, the oxide being found in volcanic districts, borax near dried-up lakes, and colemanite (calcium borate) being literally a waste product of the borax mining for which no use has yet developed.

Gay-Lussac and Thenard, Wöhler and Sainte-Claire Deville reduced the oxide by potassium or sodium, other chemists by phosphorus, magnesium, aluminium and calcium, while Duncan reduced boron chloride gas by hydrogen. Chemically, its reduction does not appear to be of extraordinary difficulty. Electrochemically, Davy electrolyzed fused boracic acid, Gores potassium borofluoride, and Faraday fused borax. All describe having isolated boron. Quite recently, Weintraub has decomposed boron chloride by hydrogen in a high-tension arc, and obtained purer boron and in larger quantity than any previous investigator. His classical paper is in the *Transactions* of the American Electrochemical Society (1909) 16, 165.

The properties of the pure boron obtained by Dr. Weintraub are exceedingly interesting. Its fusing point is extremely high, between 2,000 deg. and 2,500 deg. Cent.; it was fused in a boron nitride crucible under the pressure of its own vapor. Its boiling point is near to its fusing point; it has considerable vapor tension as low as 1,600 deg. Cent. It has a conchoidal fracture, and is nearly as hard as the diamond. At room temperature it is electrically almost a non-conductor, but at 500 deg. Cent. its conductivity has increased 2,000,000 times; at 1,000 deg. Cent. its conductivity is of the order of that of the metals. Applying moderate voltages to a cold piece, it soon warms up and makes itself a good conductor. Such extraordinary properties suggest its use for many interesting electrical contrivances, which are enumerated by Dr. Weintraub.

Other uses of boron, which have not yet been thoroughly investigated, are in the formation of boron steels and boronized copper. The former were investigated by Guillet, in France, with irregular results; in some respects, at times, the effects were similar to that of vanadium in the famous vanadium steels, at other times the results were different. The uncertainty may have been due to irregular composition of the ferro-boron alloy used. A great amount of investigation should be done on this line, first in making a reliable quality of ferro-boron, and second in using it systematically in various qualities of steel. The question of boronized copper is in a still greater state of uncertainty. Boron or even boron sub-oxide ( $B_2O_3$  or perhaps boron saturated with  $B_2O_3$ ) added to melted copper enables a perfect copper casting to be obtained of practically 100 per cent electrical conductivity; a trade product sold as boronized copper has similar effects in producing sound copper castings. These results are only the beginning of an extensive field of investigation of the effects of small amounts of boron on metals and metallic alloys. They will certainly lead to important metallurgical discoveries and improvements.

In metals and alloys boron can act chemically as a purifying or refining agent to remove oxygen, nitrogen, and perhaps sulphur, phosphorus, and dissolved oxides, while in larger amount it acts metallurgically as an alloying element. In the latter respect it forms true alloys, such as the ferro-boron alloy, which is an article of commerce. The possibilities of extensive use in molten metals and alloys are great, but mainly dependent upon systematic metallurgical research in properly equipped laboratories.

The production of the metal and its alloys also needs expert attention. For use in steel, a good uniform quality of ferro-boron is needed, and the manufacture of this in satisfactory uniform quality has not yet been mastered. Some years ago, the Pacific Coast Borax Company offered a prize of \$500, to be awarded by the American Electrochemical Society, for a practical electric furnace method of producing ferro-boron directly from calcium borate (colemanite), a waste product of the borax mines. A few years later the prize money was returned by the society to the company as not having been earned, although several attempts were made at it. For use in copper, brass and bronze, a cupro-boron alloy answers as well as having pure boron. One

method of making this is being tried, and the product is giving some very satisfactory results. Improved and more certain means of getting boron into copper are needed, and could probably be found by a moderate amount of careful investigation. As for pure boron, and the fascinating possibilities dependent on its remarkable properties, Dr. Weintraub's method makes the product, but at considerable expense, and a cheaper, easier method is a great desideratum. If such is found, boron will certainly occupy an important place among the useful metals.

#### CHROMIUM.

This element is also common and abundant in nature, and rare and expensive as a metal. Chromite, containing 34 per cent of chromium, costs normally \$20 to \$25 per ton, while the ferro-chromium alloy produced from it sells at \$100 to \$550 per ton, according to the per cent of chromium and carbon contained. But pure chromium, carbon-free, is produced only by reduction of chromium oxide by aluminium, and commands 75 cents per pound. The use of chromium in steel is rapidly extending to all varieties of extra hard and high-speed steel, but the use of pure chromium is limited by the high cost of its production and our lack of knowledge of how to handle it and of its possible useful effects. For example, chromium electroplating is white and durable, and for many purposes may be superior to nickel and almost equal to platinum plating, but the technique of always getting perfect plating has not been satisfactorily mastered. Cobalt-chromium alloys have been made which have some of the remarkable properties and uses of high-speed tool steel (stellite alloy of Mr. Haines). This is an excellent example of totally unexpected and valuable physical properties being discovered by systematic investigation. These alloys, however, must be made from pure chromium and not from ferro-alloy. How many other remarkable alloys yet remain to be discovered by patient and intelligent investigation no one knows or can even guess.

As for the methods of reduction, ferro-chromium alloy carrying high carbon (6 to 8 per cent) is produced quite cheaply in crucibles, cupola furnaces, blast furnaces, or electric furnaces. Low-carbon ferro-chromium commands three to five times as high a price, because of the difficulty of decarbonizing the raw product. It is very much to be hoped that tests will be made in the electric shaft furnace to see if it is not possible to produce directly from the ore a low-carbon product. The thing has been done in the case of pig iron, producing a low-carbon product which is called pig steel; there is no inherent impossibility in similarly mastering the conditions for producing directly the low-carbon ferro-chromium. The present prices of the two products, \$100 and \$500 per ton respectively, would warrant great efforts in that direction.

Similarly, chromium is not a difficult metal to reduce to the metallic state, but it is a difficult question to find the proper flux and to keep carbon out of it. Goldschmidt reduces it by aluminium; electrolysis of its fused salts is difficult because of their melting points. If electrolysis of aqueous solutions of chromium salts could be satisfactorily controlled, so as to produce heavy deposits, this might open the door at once to cheap and pure chromium. Electrolysis of molten relatively fixed salts in which chromium oxides are dissolved (similar to the Hall aluminium bath) is not a hopeless proposition. The chromium would be plated solid, however, on chromium cathodes, since the working temperature would be below the melting point of chromium.

The metallurgy of chromium is full of attractive possibilities, and the usefulness of pure chromium in the field of alloys is only beginning to be scratched; the scratching, however, is proving very much "worth while."

#### TITANIUM.

Our friend, Mr. A. J. Rossi, and the Titanium Alloys Manufacturing Company of Niagara Falls are the *alpha* and *omega* of the titanium industry. Nearly fifteen years ago my first introduction to Mr. Rossi was in the historic barn at Niagara, the cradle of so many of the Niagara Falls industries. Mr. Rossi was running the electric furnace and Mrs. Rossi was in the little laboratory making the necessary analyses.

Everyone knows of the enormous masses of titanic iron ore in northern New York and Canada, which contains so much iron and so little sulphur and phosphorus, that every blast furnace would be glad to get it if it was not for the titanic oxide, which makes it so unworkable that you could not give it away to them. Mr. Rossi tried first to extract the iron only, throwing away the titanium in the slag, but that was not profitable. He then turned to producing ferro-titanium alloy for use in steel and cast iron, and by indomitable perseverance has made that a success. A finely written booklet of over 100 pages, published by his company



and to be had for the asking, tells the whole story, so why take up time to rehearse it here?

In addition to titanium treatment of steel, to deoxidize and denitrogenize, this company also makes a specialty of titanium-treated aluminium bronze, also of titanium-treated bronzes and brasses of various compositions.

With titanite iron ore carrying 10 to 15 per cent of titanium as cheap as iron ore, and if iron-free material is required, rutile, 60 per cent titanium, at 5 to 7 cents per pound, there is no lack of cheap raw material. If uses are found for pure titanium, however, some other than the electric furnace must be used to reduce it, because, in absence of iron, titanium carbide would result. The methods for producing pure titanium are, like its prospective uses, still in the future, but they nevertheless are worth study and work. One can buy titanium metal now at about the price of silver, but if the problem were properly faced it could probably be made as cheaply as chromium.

#### MOLYBDENUM.

Molybdenum sulphide,  $\text{MoS}_2$ , 60 per cent molybdenum, looks almost exactly like graphite, and is about as widely distributed. Normally, it can be purchased as 90 per cent concentrates at 25 cents per pound. This would make the raw material for one pound of molybdenum cost nearly 50 cents; the selling price of the metal is about \$2. This leaves a large margin to pay for reduction.

However, the principal need of the molybdenum industry is a better utilization of its sources of raw material. The deposits have not been, in general, properly prospected or opened up, and then not properly worked. They are usually low-grade propositions, with 5 to 10 per cent of molybdenite disseminated through hard rock. This calls for careful study of crushing and concentrating methods, so as to minimize waste and loss. In most cases, the actual treatment falls far short of this, and possibly half the molybdenite in the ore is lost. The producers of the concentrates are being paid high prices for their material, but the market is limited and dull. If molybdenite were sold cheaper, there is little doubt that ferro-molybdenum, 50 to 85 per cent molybdenum, could be sold at half its present price, and the uses of molybdenum in steel correspondingly increased. New uses have also been found, such as the molybdenum wire so useful in electric resistance furnaces. This wire is scientifically very useful in that it resists the alloying action of many liquid metals even at very high temperatures. Dr. C. G. Fink of the Edison Lamp Works has studied these notable physical and chemical properties, and has described them in the *Transactions of the American Electrochemical Society* (vol. xvii., page 229, 1910).

#### ZIRCONIUM.

We may mention this element, which, as metal, is rare enough, but whose oxide has recently been found in considerable abundance. The familiar mineral zircon is the silicate, containing nearly 50 per cent of zirconium, but it is found only in limited amount. In the last ten years the oxide, baddelyite, has been found in large quantities in Minas Geraes, Brazil, running 75 to 95 per cent pure, giving 50 to 75 per cent of the metal. This source is now so common that it sells at 4 to 5 cents per pound, and is being used in large quantities as a refractory material, on account of its high melting point (2,000 deg. Cent.), high resistance to all kinds of slags, low thermal conductivity and low coefficient of expansion.

The metal, however, is almost an unknown quantity. It has been obtained by the action of potassium or sodium on the anhydrous fluorides. Fused, it is white, density 6.4, melting point 1,500 deg. Cent., hard enough to scratch quartz. Ferro-zirconium has been made in the electric furnace and used in small amounts in steel with rather indefinite results. And yet, if some very useful proportions of zirconium were discovered, the metal could undoubtedly be prepared at a reasonable price—only a fraction of the \$5 per ounce now asked for it as a chemical curiosity.

#### CERIUM.

There is a peculiar interest attaching to this metal and its close associates, from the fact that hundreds of tons of fairly rich cerium material is lying on the waste heaps outside of the incandescent mantle factories. The thorium ore used by these factories is monazite—a phosphate of the cerium earths plus thorium silicate. On extracting the thorium, the residue is worthless for mantle fabrication. It is known as "commercial cerium carbonate," and contains cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, yttrium, ytterbium, a little thorium, and considerable alkalis, iron, phosphoric acid and silica. By treatment with acids, precipitation of the rare earths, and ignition, a chocolate-brown mixture of oxides of the rare earth is obtained, in which cerium oxide predominates, and

which contains nearly 50 per cent of metallic cerium. When this mixture is reduced directly, without further separation, to the metallic state, an alloy of the rare earth metals is obtained which is known as mixed metal (mischmetal) or impure or commercial cerium. The composition of mischmetal naturally varies, but may be taken as approximately 30 to 50 per cent of cerium, 15 to 25 per cent of lanthanum, 10 to 15 per cent of the didymiums, up to 20 per cent of the yttrium metals, and 1 to 5 per cent of thorium.

An immense amount of laboratory and practical work has been expended on the production of mixed metal and of purer cerium. Prof. Muthmann and his students in Munich and Alcan Hirsch in the United States deserve particular mention for their articles, in *Liebig's Annalen* (1902 to 1910) and *Transactions American Electrochemical Society* (1911) 20, pp. 1-102, respectively. Dr. Auer von Welsbach was the pioneer in the commercial manufacture and use of mischmetal. Annoyed by the sight of heaps of the cerium residues around his mantle factories, he experimented with their reduction to mischmetal and with the possible uses of the latter. Finding that it gave off sparks when scratched he conceived the idea of using it in automatic lighters, but found that it sparked far too feebly and unreliably to be practical. He then thought that if he purified the cerium it might give sparks more freely, but on making the purest cerium he found it to spark less than the impure metal. Turning in the opposite direction, he took mischmetal and added to it alloying metals not of the rare earth class, and found that they increased the sparking property. Iron, for instance, when increased to 30 per cent gave an alloy with remarkable spark-giving properties, such as make it most efficient and reliable in automatic lighters. This has formed the basis of the "pyrophoric alloy" industry, since although other metals have similar effects the 30 per cent iron alloy is probably the best sparking alloy, for general use, so far made.

The electrolysis of fused cerium salts, double chlorides or double fluorides, to give the melted mixed metal is carried on on a large scale in Austria at Trebach, in Germany near Berlin, and was commenced in the United States, in 1916, near New York City, by Mr. Hirsch and his associates. The technique is not easy to master, and all the works keep their operations as secret as possible. The principal difficulties are the resolution of deposited metal, metal fog, and scattering of the metal as fine globules or "metal-mush" through the electrolyte, making it difficult to unite the metal to one melted mass. Since the latter trouble is largely due to surface tension, a study of this property, particularly how it can be diminished, might help in overcoming the difficulty. As an example of the opposite effect, the cupeling of lead on a bone-ash muffle depends absolutely, for its success, on the surface tension of the molten lead. But, metallic tellurium, in quite small percentage, decreases the surface tension of the lead so greatly that the metal wets the cupel and cupellation is rendered impossible. Arsenic, on the other hand, increases the surface tension of melted lead, and is therefore purposely added to it, about 0.25 per cent of it, to lead being made into lead shot, in order to make rounder shot.

A physical investigation of such effects on cerium might well assist in overcoming the scattering of the metal in globules in the electrolyte. Another direction in which improvement might be made would be the careful study of the eutectics of mixtures of cerium salts with barium salts, so as to find an electrolyte of lower melting point in which the losses by re-solution of deposited metal would be less than they are at present. Another possible improvement would be the finding of an electrolyte which would dissolve cerium oxide or the mixed oxides directly, and give metal by electrolysis. Such a bath has been discovered for aluminium oxide, and a long experimental search for a similar bath for the cerium oxides would be amply justified.

The possibility of using the 30 per cent iron alloy as a melted cathode, and enriching it in cerium by electrolysis, might be considered. If we had the fusing point curve of cerium-iron alloys we could draw some useful conclusions in this direction. The addition of small amounts of other metals to the bath, so as to produce other useful cerium alloys directly, might facilitate the electrolytic operation. Furthermore, experience with the process, particularly by those familiar with the electrolysis of molten baths for sodium, magnesium or aluminium, will very probably lead to considerable improvements and reductions of cost.

The uses of cerium and particularly of its alloys are sure to increase, and may attain considerable proportions. It has been proposed by Borchers as an addition in small quantity to aluminium, to improve its properties. But the large use will always be the pyro-

phoric alloys, which have so largely replaced matches. Before the European war, over 3,000 workers were employed in Austria in this industry of pyrophoric alloy and automatic lighters. Mistakes were made in the early days of the industry, and some alloys put in lighters which crumbled to pieces by the time the apparatus reached Australia, but continual improvement was being made, until a satisfactory substitute for matches was attained. The improvement most needed in the pocket lighting apparatus is to be able to dispense with alcohol or similar liquid; a wick impregnated with a solid combustible which can be ignited by a pyrophoric alloy, would give a great impetus to this art.

## SCIENTIFIC AMERICAN SUPPLEMENT

Founded 1876

NEW YORK, SATURDAY, SEPTEMBER, 30th, 1915

Published weekly by Munn & Company, incorporated.  
Charles Allen Munn, President; Frederick Converse Beach,  
Secretary; Orson D. Munn, Treasurer;  
all at 233 Broadway, New York

Entered at Post Office of New York, N. Y., as Second Class Matter  
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Scientific American Supplement (established 1876) per year \$5.00  
Scientific American (established 1845) . . . . . 3.00  
The combined subscription rates and rates to foreign countries including Canada, will be furnished upon application  
Remit by postal or express money order, bank draft or check

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