IRON AND CALCIUM.

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Now that calcium has become available for experimental purposes, and could no doubt be produced cheaply enough for commercial use, provided there were a large demand for it, any new experiments with this metal, although they have yielded results of no constructive value, may yet contribute something to our all too scanty knowledge of the properties and uses of this interesting element. It is with this in mind that an account of the experiments which follow is presented. One of the most promising fields for the use of calcium would seem to be in metallurgy, particularly in the metallurgy of iron, where it might prove an efficient substitute for the deoxidizing agents—silicon, manganese, and aluminum. In addition to its action as a deoxidizing agent, calcium might be expected to be of value in removing sulphur and phosphorus from iron. A proposal to use calcium for these purposes raises the question of the extent to which any excess of calcium will alloy with the iron, and its effects upon the latter metal. These are the questions concerning which some preliminary experiments have been made.

Four attempts were made to form alloys of calcium with iron by fusing together the two metals. In order to prevent oxidation of the calcium before the iron reached its melting-point, the calcium was hammered into a cavity drilled in a cylinder of pure iron, and an iron cap either screwed or hammered tightly into the opening, so that it would have required an internal pressure of several hundred pounds per square inch to force out the cap. The cylinder was placed in a crucible of Acheson graphite lined with magnesia, tightly covered with the same materials, and heated in an electric furnace of the resistance type until the iron melted. Owing to the low density of calcium, the weight of this metal used in each case was small.

	I.	II.	III.	IV.
Weight of calcium taken	1.6	4.5	6.0	14.3
Per cent. of calcium taken	0.23	1.4	0.77	3.78

The results as to the alloying of the two metals were uniform—no calcium was found in the melted iron. Two changes in composition were, however, made by the calcium. In IV the content both of silicon and of carbon was increased to 0.32 per cent. silicon and 0.218 per cent. carbon. The same iron melted under like conditions, but, without the calcium, contains 0.01 to 0.09 per cent. silicon and 0.03 to 0.04 per cent. carbon, so that the actual increase was 0.83 gram silicon and 0.65 gram carbon. The first thought would naturally be that this increase of silicon and carbon was due to impurities in the calcium used, but this would require that metal to contain 5.8 per cent. silicon and 4.5 per cent. carbon. The gas evolved by the action of this calcium on water had only the faintest odor, and burned with a non-luminous flame, indicating the absence of any considerable amount of calcium carbide. The calcium came from Germany and was not analyzed by the writer, but analysis of similar metal by B. Larsen[1] gave 0.11 per cent. CaC_2. The only tenable inference seems to be that the silicon and carbon are reduction products of the action of the calcium upon silica present as impurity in the magnesia lining, and upon carbon monoxide in the atmosphere within the crucible. In previous attempts to produce alloys of iron high in aluminum, by melting together the two metals in a similar crucible buried in a carbon resistor, the reducing action upon the carbon monoxide was so great as to form large amounts of aluminum carbide. It was therefore expected that calcium would act similarly, and it is only surprising that the extent of this action was not greater. In this connection the action of calcium upon carbon dioxide was tested by kindling a thin piece of the metal in the air, which was difficult to do with the highest heat of a Bunsen burner, and plunging it into a jar of the gas. It burned brilliantly, much more so than in air, leaving as solid products, lime, calcium carbide and carbon. A further attempt at alloying iron and calcium was made by heating 2 grams of calcium within a cylinder of pure iron for seventeen hours at 850–880°. The calcium melted, but no trace of alloying was found. C. Quasebart, of Aachen,[2] also obtained negative results in several attempts to alloy calcium with iron.

As a last resort in the endeavor to alloy iron with calcium, iron oxide was reduced by calcium filings in the presence of excess of calcium. The charge, consisting of 42 grams calcium filings, 60 grams pulverized Fe_3O_4, and 20 grams of calcium in lumps,

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[1] Chem. Centr. 2, 1466 (1905).

[2] Electrochem. Met. Ind. May, 1906, p. 190.

was put into a magnesia crucible. This was enclosed in a strong steel cylinder, devised by Professor C. F. Burgess for firing thermite and similar charges under great pressure, and kindly placed at the disposal of the author. The charge was fired electrically by means of an iron fuse-wire. The reaction was very vigorous and resulted in a metallic ingot and several small pellets. In cold water gas was slowly evolved from the metal at a few points on the surface and calcium hydroxide was formed. For analysis a small piece was heated for three hours in water until all evolution of gas had ceased. It was then washed, dissolved in hydrochloric acid, and found to contain 0.3 per cent. of calcium. Although this amount of calcium came from the interior of the mass of metal, in view of the failure of all other attempts to make an alloy it seems probable that the calcium was imprisoned by the sudden cooling after reaction occurred and held mechanically, not alloyed with the iron.

The diffusion of phosphide of iron through solid iron at high temperatures has been pointed out by J. O. Arnold.[1] Experiments were tried to see if calcium, when heated in contact with iron containing phosphorus and sulphur, would diminish the amounts of these elements sufficiently for the change to be detected by the microscope. To prepare metal for this treatment, coarsely pulverized electrolytic iron was mixed with sulphur and placed in a magnesia-lined crucible, while red phosphorus was enclosed in a cylinder of pure iron and placed in another crucible; both were melted in the electric furnace.

	For sulphur.	For phosphorus.
Weight of iron in charge	372.4 grams.	438.62 grams.
Weight of non-metal in charge	7.6 "	13.5 "
Percentage of non-metal in charge	2	2.76
Percentage of non-metal found	0.3	1.96
Weight of non-metal combined with iron	1.13 grams.	8.62 grams.

Holes were drilled in the ingots; into these were put 5.0 grams and 7.3 grams of calcium, respectively, and the openings were closed by caps of pure iron. The ingots were packed in powdered magnesia in a crucible, and heated five hours, at 1200–1300° in a gas furnace. They were badly oxidized, particularly at the tops. All calcium had vanished and the ingot had become perfectly homogeneous, except that the boundaries of the cavity which had contained the calcium could still be distinguished.

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[1] J. Iron Steel Inst. 1894, I, p. 107.

Each ingot was of the same structure throughout, the caps of pure iron having the same appearance under the microscope as the rest of the ingot. Dark areas, probably of phosphide eutectic, were distributed quite uniformly throughout the ingots. The calcium in this experiment was probably oxidized partially, and perhaps wholly, by oxide of iron.

In the same way calcium was melted with iron containing phosphorus and sulphur. Eight grams of calcium removed all of the 0.37 gram of sulphur present in one ingot, and 11 grams of calcium removed 0.61 gram out of a total of 6.04 grams of phosphorus present in the other ingot, thus reducing the percentage of the latter element from 1.96 to 1.56.

These experiments show:

1. That iron and calcium do not form alloys.
2. That by the reduction of the oxides of carbon the latter element may be introduced into fused metals to which calcium is added.
3. That any commercial application of calcium to the removal or phosphorus from iron is impracticable.

The above observations were made incidental to an investigation of iron alloys, now in progress under a grant from the Carnegie Institution.

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THE CONSTITUTION OF PARIS GREEN AND ITS HOMOLOGUES.

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INTRODUCTION.

COPPER aceto-arsenite, under the names of Paris green, Schweinfurt green, and many others, has been a commercial product for nearly a century. The first contribution to its chemistry that I am able to find was made by Liebig.[1] The first definite statement in regard to its composition was made by Ehrmann,[2] working in Liebig's laboratory, who found it to consist of 3 molecules of copper meta-arsenite crystallized with 1

[1] Liebig u. Poggendorf's Handwörterbuch der reinen und angewandten Chemie, 1848, 703.

[2] Ann. 12, 92.