

THE SURVIVAL OF PLASMA CHEMISTRY

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ABSTRACT

The role of plasma chemistry in the realm of scientific thought and activity is examined and suggestions are made for expansion in the future by investigating the features of currently successful operations which involve a plasma heating stage and may be less demanding of energy and space than some older processes.

An unmistakable trend is taking place today which can be damaging to everyone interested in plasma chemistry on any level. Industrial interest in plasma chemistry is waning. True, a mood once existed, largely during the 1960s, that research in plasma chemistry was going to give birth to a far reaching 'great leap forward' in the chemical industry. With little forethought and almost no contact between the research minded chemist, the chemical engineer, and the plasma equipment manufacturer, plasma chemistry researchers and plasma chemistry research groups sprang up all over the industrialized Western countries and in the Soviet sphere as well. In the USA during this time almost every progressive large industrial chemical firm was involved to some extent. It would have been risking for itself the fate of the dinosaurs if it did not have at least a small group of people doing plasma chemistry. A large amount of laboratory scale plasma equipment was sold and a large number of 'homemade' plasma units went into operation. In retrospect, this broad flurry of activity, largely undirected toward logical goals, and uncommunicative with the realities of scale and economics, seems unrealistic.

The present situation is a mood that plasma chemical research is a waste of time, effort and money. That is equally unrealistic. As so often happens in human history, the swinging of the pendulum has taken us from one extreme to the opposite extreme.

The fact is that the early 1970s have witnessed the development of the first publicly acknowledged, large scale, profit making industrial process based on a plasma chemical step. There is every reason to believe that more such processes will follow. We must realize, however, that if progress in knowledge of plasma chemistry is to be made, funding is required. In a profit oriented economy, funding is available only if profit is potentially to be made from the funded research. From the standpoint of industry, profits accrue from large scale operations which result in significant value added as a consequence of the operations. Therefore, it must be recognized that, whereas industrial scale operations can never come to fruition without an adequate base of research and development activities, so research and

development activities cannot look forward to continuing support in the absence of robust industrial scale plasma chemical operations.

It is my view that a collection of guidelines of practical orientation should be kept in mind by the researcher when he chooses a project. These guidelines are the same as those that would inevitably be discussed in the board room or general manager's office at some future time when the researcher's efforts have shown sufficient progress to allow consideration of increased funding or scale up or both. In effect, what I am asking is that the researcher put himself in the place of the marketing manager, the technical director, the board of directors, and the stockholders, as the case may be. This is not to say that the researcher should become an economist, although I can see some advantage in that. It simply means that he should keep in mind the potential industrial viability of a process from its inception. Economics aside, I see the following elements which must be considered in the evaluation of the industrial merit of a particular plasma chemical reaction. They are: Simplicity, Yield, Quality of product, Consistency of product, and Demand for product.

Let me discuss these guidelines or criteria one by one. First, *simplicity*; as we all know human beings are fallible. Let us allow ourselves the egotism to say that as the project passes from the researcher's hands, through development and plant engineering, to day-to-day operation, the chance for error becomes increasingly greater and the likelihood is diminished that repairs can be made or corrective action taken on the strength of a thorough knowledge of the science involved. Even if this were not true, just from the standpoint of simple probability, the more things that have to be done correctly the more opportunity there is for something to go wrong. We Americans call it Murphy's law—"If anything can go wrong, it will". Thus, as in all phases of industrial chemistry a simple process is a good process; a good process is a simple process.

Yield. With today's technology and in the foreseeable future, plasma operations are not particularly cheap. At some point in the process 100 per cent of some feedstock is exposed to the plasma. If this step results in 100 per cent product, or intermediate, or whatever, this is excellent. If it results in 50 per cent effectiveness, the unit cost of plasma processing is, to a first approximation, immediately doubled. The ratio of product obtained to reagent processed is very important. It is difficult to see how a plasma step with, for example, ten per cent yield can ever be economically justified.

Quality of product. This is one area which can cancel the negative effects of unfavourable situations with regard to simplicity and yield. If plasma processing produces a product which has no counterpart, or is in some way demonstrably superior to similar products made in a conventional way, processing complications and relatively small yields might be tolerable.

Consistency of product. Are high quality, uniform starting materials available? Does the process lend itself to a design which permits every portion of the feed stream to see the same enthalpy/temperature history? If the answers are positive, these elements go far in determining the consistency of the final product. Plasma operations in which the reagents flow through the plasma can enjoy an inherent advantage over conventional high temperature furnacing.

Demand for product. If a need for processing at higher temperatures exists, for instance, with regard to some material of commerce, or if the materials of commerce available at present are in short supply or suffer from inconsistent availability, an opportunity may exist for a plasma based process to fill the demand.

The project which has been brought to industrial scale reality at TAFE is the production of zirconium dioxide from zircon sand. The critical step is direct dissociation of the zircon sand into a zirconia-silica mixture in a streaming thermal plasma. Let us, then, with the great benefit of hindsight, examine this process in the light of the above mentioned criteria as if we were deciding whether to mount a significant research campaign toward development of such a process.

Simplicity. Zircon sand, zirconium silicate, must attain a temperature of at least 1775°C to produce dissociation. Dissociation is spontaneous at this temperature. Above 2700°C, all components are in the liquid state. The phase diagram suggests that a zirconia rich phase with a very few per cent of silica, and a silica rich phase with similarly low concentration of zirconia, will be produced. Simple enough.

Yield. There is nothing to indicate that the reaction will stop short of completion, provided every particle of zirconium silicate can be brought to the required temperature and quenched properly. Of course, we shall have to pick a particle size range large enough to avoid wasteful vaporization and small enough to permit heat affection of each particle throughout. We know that too large a particle tends to pass through the plasma with a residual kernel of starting material in its centre. It would appear that yield, then, will depend only on the proper choice of a starting material and an adequately large plasma processing unit.

Quality of product. It is difficult to say in advance exactly what the nature of the product will be, but its quality will certainly be in part dependent upon the quality of the raw materials available. Here we are extremely lucky. Zircon is available from a variety of sources in purities approaching 99.7 per cent zirconium silicate.

Consistency of product. Conventional processes for making zirconia involve the addition of some fluxing agent and the subsequent dissociation of this 'contaminated' zircon in a conventional arc furnace or calcining kiln. The 'contaminants' are removed with varying degrees of success and the degree of heat affection during the dissociation step is variable. It depends upon the geometry of the furnace and the location of individual regions of the batch. We propose to dissociate the zircon directly without adding any 'contaminants' and to effect the dissociation in a flowing stream of very limited dimensions. It would appear that our approach offers a maximum possibility for batch to batch consistency.

Demand for product. There are well established uses for zirconium oxide. The industry is of a modest scale, compared to that of commodities like sulphuric acid and chlorine. Discussions with users of zirconium oxide have made it apparent that a uniform product with batch to batch consistency would be welcome in the industry.

Thus it would seem that our proposed project to make zirconium dioxide fits rather well all of the criteria for determining the merit of a proposed

plasma chemical system. It is not difficult to understand why a certain element of success has been achieved.

Of course, it is unreasonable to expect an economically viable industrial chemical process to be carried out in laboratory scale equipment capable of processing only a few pounds of material per hour. Large scale equipment must be available for plasma treatment of at least hundreds of pounds per hour before any consideration can be given to entering the marketplace. Happily, such equipment is now available without great capital investment or excessive space requirements. Uniformity of heat affection is an accomplished fact, and rapid heat-up with extremely rapid quench are inherent in the operation of the plasma furnace.

So, enough of hindsight and pedagogical example. The decision was actually made in 1970 to pursue development of a process based on plasma dissociation of zircon, followed by an aqueous caustic leach to remove silica. Laboratory studies were carried out for about one year and by the autumn of 1971 a 100000 pound per year pilot plant was in operation employing a two-stage leach system. In the first stage leach, twice the amount of sodium hydroxide required for the formation of sodium metasilicate was reacted with dissociated zircon to produce 95 per cent zirconia, 5 per cent silica. The spent leach liquor was removed and a fresh charge of sodium hydroxide was employed in the second stage leach, reducing the silica content to less than one per cent. Since that time, reliable plasma treatment at approximately 0.8 kilowatt hour per pound of zircon has become a routine operation and has permitted the workers to concentrate on further refinement of the leach step.

It was found that a material containing less than two per cent silica could be produced in a single leach step and this material was found to be satisfactory in a number of applications. Moreover, the sodium hydroxide to dissociated zircon stoichiometry could be reduced to unity. Thus, the two-stage leach was simplified to a single leach and sodium metasilicate is now produced directly in this single step as a co-product. The metasilicate is an article of commerce with a wide spectrum of uses in industry. The project has enjoyed its share of good fortune in addition to these engineering improvements. The rapid quench of the completely liquefied zircon produces zirconium dioxide crystallites which are very uniform and in the range 0.1 to 0.2 micrometres. The concomitant surface area is 7 to 9 square metres per gram. This unique structural quality has provided three substantial advantages in the material. First, in the ceramic colour industry, which depends upon solid-solid reactions between oxides to develop refractory colours, the intimate mixtures which can be obtained lead to easily produced intense colours. Second, the inherent porosity resulting from removal of interstitial silica from the dissociated mixture produces lighter and, consequently, less expensive zirconia ceramic bodies. Third, the high surface area of the zirconium dioxide renders it unusually soluble in boiling sulphuric acid. Hence, the oxide can be conveniently employed as a starting material for zirconium chemicals. During the autumn of 1972, a decision was made to scale up the process to provide capacity of over one million pounds per year of zirconium dioxide. This scale-up involved the provision of large scale zircon storage facilities and the materials handling equipment to provide

for continuous, round-the clock, operation of the plasma furnace. Additionally, a new leaching facility was installed on a sufficiently large scale to process on a one shift basis the entire production of the plasma step operating on a twenty-four-hour basis. The leaching facility went into operation earlier this summer without incident and has repeatedly dramatized the reliability advantage of simplicity of approach. Yields based upon zircon sand and sodium hydroxide employed approach 100 per cent and it is fair to say that at this modest level of operation, the plasma zirconia process is already economically competitive with several existing conventional processes operated at substantially larger scale. Development activities are continuing around the plasma furnace itself and it is possible to say that the future holds the likelihood of direct competition by plasma with much electric furnace technology and even some gas fired calcining processes. Without doubt, the first penetrations into these areas of conventional technology will be in cases where temperature limitations have an adverse effect on processing time and lead to excessive maintenance requirements.

Consequently, we see the survival of plasma chemistry assured and the day of robust industrial plasma chemistry at hand provided researchers in the field concentrate their efforts on those projects which can take rational advantage of the inherent characteristics of the equipment available and the advantages of plasma processing in general. I need not belabour these in such knowledgeable company. Let me just mention that plasma operations thrive on requirements for the attainment of temperatures in excess of 2000 Kelvin, minimal capital expense and commitment of factory space, uniform heat affection, and rapid heat input and quench. Plasma treatment also offers a flow process instead of a batch process.

There are a number of specific applications of plasma techniques in chemistry and chemically related industry which can even now be identified. I will enumerate a few of these:

Formation of double oxides from the individual oxides. It has already been noted, much to the chagrin of those who were trying to dissociate zircon at the time, that the existence of alumina in a silica bearing mineral leads to the formation of mullite, the most stable and intractable form of aluminium silicate. In like manner, it would appear that a number of double oxide systems should be studied to see if economically justifiable processes can be developed which start with physical mixtures of the oxides and produce the desired chemical combination. Zinc type ferrites have been produced from mixtures of iron and zinc oxides in plasma with the unexpected bonus, presumably due to the rapid heat up and quench, of reduced loss of zinc oxide through vaporization.

Direct dissociation of sulphide ores. The present emphasis on non-polluting processes has generated substantial interest in the direct dissociation of sulphide ores to remove sulphur in elemental form. Thus, the obnoxious byproducts of sulphur dioxide or hydrogen sulphide could be avoided and pollution reduced accordingly. Huska and Clump¹ have shown that decomposition of molybdenum disulphide is possible in plasma and it would appear that other minerals such as pentlandite, an iron-nickel sulphide complex, and chalcopyrite, a copper-iron sulphide, might lend themselves to plasma processing to produce valuable products. A word of caution and

encouragement to the researcher. Here, as with other systems, it must be recognized that laboratory results achieved with lesser heat affection may not always indicate qualitatively what can be expected from large scale operations offering longer heat zones of higher intensity. Thus, positive, encouraging results on the laboratory scale may be looked upon as assurance that at least equivalent qualitative results and superior economic results will be gained from operating on the large scale. However, negative or discouraging results on the laboratory scale do not necessarily indicate that the proposed reaction cannot be carried out satisfactorily on a larger scale. This is especially true in cases where one suspects that the negative results in the laboratory are due to insufficient enthalpy having been transferred from the plasma to the materials being processed. In very general terms, if thermodynamic analysis indicates that the desired reactions should take place to completion at temperatures between 2000 and 3000 K, it is entirely possible that the economically attractive processing of hundreds of pounds per hour of the material can be achieved in a large scale plasma furnace. An attempt to process the same material at a rate of one pound per hour in ordinary laboratory plasma equipment, may give results which are uninspiring at best.

Spheroidization. This technique involves simply taking jagged particles of some metallic or non-metallic refractory material, and feeding them through a plasma so that each individual particle melts and becomes spherical through surface tension effects. If the product is for some market which requires perfect spheres, care must be taken that a sufficiently long shot tower is provided to allow the particles to solidify before striking the collection surface. From the standpoint of practical application, this technique is limited to particles from 10 micrometres to one millimetre in diameter. A variant of this technique with chemical reaction can be applied in the case of silica, for instance. Here crystalline quartz can be converted to amorphous silica which can then be employed as a starting material in the fabrication of fused silica bodies. The entire area of material treatment to produce high temperature phase changes should be examined to identify candidate systems for this type of plasma processing.

Dissociation of silicates. A number of silicates other than zircon are available in reasonably high purity at low cost. Wherever dissociation is thermodynamically favoured or indicated by the phase diagram, a plasma processing step is likely to provide complete and efficient separation of the cations. Some examples of the possibilities are; rhodonite, manganese silicate, of which the dissociation in plasma was first described by Charles *et al.*²; chrysocolla, a copper silicate; and phenacite, a beryllium silicate. It is quite likely that, in at least these three cases, the silica would be rendered into amorphous form and could be leached with aqueous caustic in a process analogous to that employed for the production of zirconium dioxide today.

Direct stabilization of zirconia. Bypassing the cumbersome solid-solid reaction which must be carried out to incorporate calcia or yttria into monoclinic zirconia to provide stabilized zirconia, the same phase change can be accomplished in milliseconds by passage of a physical mixture of the materials through a thermal streaming plasma. Here again, we note the potential advantage of plasma processing as a replacement for some of the

higher temperature calcining and electric furnace operations of the present day.

Decomposition of nitrides to obtain metals. Some interesting and promising new routes to the formation of nitrides have been hinted at. A substantial amount of the information regarding these developments seems to be proprietary and unpublished. Nevertheless, if it can be shown that an inexpensive commercial route to nitride formation exists, then it is entirely likely that there will be found a place for plasma processing in the decomposition of these nitrides to obtain metals.

Vaporization of impurities from inexpensive materials. For this suggestion we need only refer to Dr Bonet's thesis³, in which he suggests that Bayer alumina can be processed in plasma to evaporate sodium oxide and thereby produce a purer, more valuable form of aluminium oxide.

The above list of possible types of systems for commercial exploitation using plasma techniques is a modest but significant one. It will be seen that their requirements are to some extent consistent with the general advantages of plasma operations. Repeating these, they are: intense thermal affection without great capital investment or space commitment, uniformity of heat affection, amenability to flow processing, and extremely rapid and intense heat up and quench. On the practical level, costs on the order of 10¢ per pound of the material being treated are near to hand and continuing efforts assure that this cost will be reduced as time passes.

I frankly feel that the future of plasma chemistry could be made brighter by a partial reorientation of plasma chemistry researchers toward simple and economically viable systems. Communication between researchers and the people who can provide reliable equipment for scale-up is also necessary. This symposium and others like it in the future, represent excellent vehicles for the type of communication which is required, but continuing individual contacts in the intervals between symposia are also necessary. The type of research which I have described may be inelegant, new information which contributes to a basic understanding of high temperature phenomena may or may not come to light, but the very survival of our discipline may be ensured. We are at the present time witnessing a reduction in industrially sponsored plasma chemical activities while, simultaneously, successful equipment scale-up has been accomplished and at least one economically viable process is on stream at an industrial scale. This is certainly the time for us to step back and consider seriously where we are headed as a discipline.

As Shakespeare tells us, in *Julius Caesar*, 'There is a tide in the affairs of men, which, taken at the flood, leads on to fortune; omitted, all the voyage of their life is bound in shallows and in miseries'.

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