

THE CURRENT STATE AND FUTURE DIRECTIONS OF INDUSTRIAL PLASMA CHEMISTRY

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Abstract—Some current activities in industrial scale plasma chemistry are discussed in terms of their present scale of operation, the rationale behind the use of a plasma step, and the prospects for their ultimate success. Trends in industrial energy consumption are described which are expected to accelerate the development of industrial plasma chemistry. Thermodynamic considerations in the use of diatomic gases are shown to recommend them as working fluids for plasma heating operations. Cooperation between Thermodynamicists, Heat Transfer Theoreticians, and Equipment Designers is recommended for the advancement of basic understanding as well as commercial viability of this new Chemical Engineering Unit Operation.

Almost exactly two years ago, at the September, 1973 IUPAC Symposium on plasma chemistry which was held in Kiel, Germany, I addressed myself to somewhat the same topic of which I will speak today. That is, I tried to summarize where we stand in our progress toward making plasma treatment of reagents an accepted chemical engineering unit operation. Significantly, my lecture at that time was entitled "The Survival of Plasma Chemistry", showing concern that industrial support for development of plasma-based chemical processes had been greatly reduced. For this trend to be reversed, it seemed to me that researchers in our field should begin to pay closer attention to the practical and economic reasons for undertaking plasma chemical research. A list of criteria or guidelines was presented by which the researcher could evaluate the potential viability of a proposed plasma chemical research or development program. These criteria included good yield of product from the mass of material processed, simplicity, and high unit value added as a result of the plasma step itself.

I still feel strongly that our future as an industry depends on how carefully we choose our research and development projects. However, it pleases me to say that any fears for the actual survival of plasma chemistry seem out of date and unnecessary two years later. Technology and industry now seem to be very much aware that commercial scale plasma chemical operations will grow and proliferate. Of course, all the classic reasons for considering a plasma process are still valid. It is still true that savings in capital expenditure and space requirements can be accomplished by using a plasma technique. Plasma techniques still lend themselves very well to the replacement of batch processes by flow processes. They still offer rapid heatup and quench with relatively easy attainment of reactant temperatures in the 2000-3000°C range. Conventional technology has still not found a comfortable way of attaining these temperatures in materials.

However, it is not careful attention to these possibilities or a new, incisively practical outlook on the part of researchers in plasma chemistry that seems to have insured the survival and growth of our young industry. It is rather the sudden and dramatic increase in the market value of hydrocarbon fuels that has given our discipline new importance. As M. G. Fey so thoroughly demonstrated at the National Meeting of the American Chemical

Society last September,¹ we are rapidly and inescapably headed toward an electrical economy. Increasingly, process heat will cease to be provided by hydrocarbon fuel sources and instead will depend more and more on electricity. Plasma processing is bound to receive a share of the activity as high temperature processing makes the required conversion. All the well known factors which are recognized as potential advantages of plasma processing will at various times influence decisions to replace conventional processes with plasma processes.

One advantage of processing in a plasma environment, however, has not received the attention it deserves. This advantage is the tremendous acceleration of reaction rate which is observed, especially in the case of the heat affection of refractory particulates. Significantly, it is this very problem of the heat affection of particulates that will receive much of our attention at this Round Table. This is altogether fitting, because when we consider the types of high temperature chemical activities which today depend on process heat from hydrocarbon sources, operation on particles stands foremost on the list. The potential speedup offered by plasma in this type of processing has not been given much attention in the past, probably because not very much experience had been accumulated in treating large quantities of material at high rates. There were no data to compare with conventional experience. Now, with the benefit of industrial scale plasma experience gained over the last few years, it is possible to make a few generalizations regarding the dramatic increases in reaction rate which have been attained, their effect upon throughput, and the benefit of these on the economics of high temperature processing. It reduces to this; an extremely hot environment gives very high reaction rates, very high reaction rates permit very short residence time to accomplish the desired physical or chemical changes in the material treated and very short residence time permits respectable throughput in a very small volume. Those of us who have been privileged to be intimately involved with plasma processing of particulates on a large scale have been amused at what an unimpressively small falling stream of particles can represent a production rate in the range of hundreds of kilograms per hour. Conversely, it is necessary to recognize what huge equipment is required to provide a production rate of hundreds of kilograms per hour when the retention time in a hot zone must be of the order of tens of hours to accomplish the desired reaction. It has been intuitively apparent to plasma processing enthusiasts that these advantages could be realized, but it

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has taken the recent advent of large scale plasma processing to make us recognize the full implication of the expected improvement. Let me cite two examples. Some years ago² a producer of zirconium dioxide recognized the potential advantage of thermally dissociating zircon (zirconium silicate). He exposed zircon particles less than 44 μm in diameter for 24 hr in a special high temperature kiln capable of holding 2000°C. At the end of this exposure, the zircon was "more than 50% dissociated". By contrast, plasma processing can achieve essentially full dissociation in particles 75–150 μm in diameter with residence times on the order of 3 msec. The mass of the particles which are routinely processed in plasma is a factor of ten greater than the mass of those which were processed in conventional equipment. Considering this and the great difference in exposure time, it is possible to estimate that the reaction rate has been increased by a factor on the order of 10^8 – 10^9 . Similarly dramatic results have been obtained in the production of zinc ferrites from mixtures of iron oxide and zinc oxide. It is also clear from these and other systems that improvements in product quality can result from the very short exposure time. Undesirable side reactions and reverse reactions tend to be minimized.

In summary, it appears that prospects for industrial scale plasma chemistry have brightened considerably during the past 2 yr. The improved situation is attributable to the energy situation and to the accumulation of some very gratifying data from those operations which have already been carried out on a substantial scale.

What types of activities are characteristic of today's efforts in industrial chemical use of plasma generating equipment? Listening to discussion and presentations at meetings of plasma chemists, one quickly gets the impression of two very different types of industrial application for which process heat is provided by plasma generating equipment. First there are the low temperature, low pressure processes in which ionization and the availability of free electrons are actually of significance in obtaining the desired results. The electronics industry is very conspicuous in these activities, and some serious efforts in organic synthesis are also beginning to develop. The other group of "plasma chemists", including a majority of us here at this meeting, are interested in the high temperature thermal affection of materials. We are not "plasma chemists" in the strictest sense of the phrase. The point was raised and often repeated at last year's Gordon Research Conference that we should begin to think of ourselves as a particular breed of ultra high temperature chemists. We could reserve the term "Plasma Chemistry" for those systems in which the availability of charged particles in abundance is of demonstrable significance. The distinction between what we are actually involved in and what we have historically defined as plasma chemistry is not a trivial one. Recognizing the distinction helps us to analyze our goals and to simplify our understanding of what happens in our processes.

If we can make use of a simplified model of thermal affection in a 5000–10,000°K ambient, we should be able to predict better how new proposed systems will respond. In this connection, there is ample need and opportunity for fundamental work on such things as gas–solid interactions in extreme environments. One such effort, involving theoretical heat transfer rates between a working gas and small particles exposed to the gas has been published by the Electricity Council Research Centre³ at Capenhurst, UK. As industrial plasma processes increase in number, it should be possible to make use of empirical experience in

industry to improve our understanding of the theory. Our understanding of heat transfer under the outlandish conditions we create must certainly be improved, and the technical challenge is indeed great. A concerted effort to understand fully the heat affection of materials in plasma produced gases also requires attention to the thermodynamics involved, and I suggest that these two aspects of energy transfer be considered together. This does not mean that a complicated simultaneous solution to the energetics and kinetics must be sought. Rather, the results of heat transfer calculations should be compared to those of the thermodynamic calculations and vice versa. The more comprehensive picture that emerges can then be compared to actual experience to see where the theory must be improved. All this will take a great deal of communication between researchers and industrial practitioners along with a willingness on the part of the latter to share the details of their accumulated data.

As a first easy step, the conjunction of a plasma generated stream of hot gas and a cold stream of particles or reagents can be looked upon as a simple mixing of two fluids. In this way, we approach the heat transfer problem from the other direction. In other words, we provide a picture of how effective overall heat transfer must be to produce the desired results. As an example, let us consider nitrogen as the working gas and estimate how much heat is available from it under different operating conditions. Nitrogen is an especially interesting gas to consider for ordinary calcining type operations because it is relatively inert, convenient to use as a plasma working gas, and diatomic. This last consideration has not always been fully appreciated. In a nitrogen plasma generated in conventional equipment, the predominant species is monatomic nitrogen. Ions and electrons are relatively rare unless rather extraordinary steps are taken to increase the enthalpy. Since these steps are often uneconomical and unnecessary, we should usually be content with a heat source of reasonably well dissociated nitrogen. Before the late fifties, we all learned that the dissociation energy of nitrogen had the extraordinarily high value of 170 kcal/mol. This was wrong. High temperature thermodynamicists now agree on a value of approximately 225 kcal/mol. This amazing little parcel of energy is available for the heat affection of materials or reagents whenever two nitrogen atoms recombine. Of equal importance is the fact that the energy is rendered very much in the same way as a latent heat, substantially without reduction of temperature. Consequently, energy transfer takes place from dissociated nitrogen while the heat transfer driving force remains essentially undiminished. The following two tables have been prepared from thermodynamic data alone. They illustrate, for the case of nitrogen, how the degree of dissociation and the availability of sensible heat change with temperature in the range of interest to us.

In Table 2, assumptions of three different nitrogen discharge temperatures have been made. The lower the

Table 1. Effect of temperature on the dissociation and enthalpy of nitrogen

Temp. (°K)	Per cent Dissoc.	kWh M ³	Btu lb
7000	45	8.4	11,250
7500	65	11.2	15,000
8000	82	13.8	18,450

Table 2. Nitrogen—kWh available per M³

Discharge temp. (°K)	Initial temperature (°K)		
	7000	7500	8000
4000	7.4	10.3	12.8
5000	6.3	9.1	11.7
6000	4.9	7.7	10.3

discharge temperature, the more efficient the removal of sensible heat from the nitrogen by the process stream. Obviously, this table bears greatly on the heat transfer problem. Perhaps not so obvious is our recent recognition that great gains in efficiency can be realized by the proper design of reagent feed systems to take advantage of the entire volume of the streaming thermal plasma. There is a great need, then, to merge theory with practical operating and design experience. Only with this kind of communication will our understanding become clearer.

Let us now review the current situation in industrial scale plasma processing by considering a few of the operations which have been discussed publicly in recent years. It must be recognized that other projects are being carried out on a proprietary basis behind closed doors.

The large scale dissociation of zircon in plasma as the first step in a process to produce zirconium dioxide, has been carried out in the U.S. since 1970. This would appear to be the plasma process which is most advanced in its efforts to attain full commercial potential. In July of 1973, the process reached a scale at which the economics appeared favorable. As was noted in *Chemical Week*⁴ early this year, Associated Minerals Consolidated, a large Australian producer of zircon, is considering a substantial scaleup of the process. All indications are that AMC is proceeding with its scaleup plans.

A large, comprehensive program to produce molybdenum metal from molybdenum disulfide in plasma is being carried out in Canada at the Noranda Research Centre and McGill University. Dr. Gauvin, who heads this project, has pointed out that the process development is burdened by very stringent purity requirements. Nevertheless, the thoroughgoing analytical approach which is being employed here will certainly provide the maximum probability for success in these endeavors.

Another program in extractive metallurgy is under way at the Electricity Council Research Centre. Dr. Lawton's group is investigating the reduction of titanium tetrachloride to titanium metal with sodium. Their use of a plasma as the source of heat in the reaction zone provides some interesting potential advantages. First, complete reaction can be achieved in milliseconds in a flow process. Also, the formation of the products in an ultra high temperature environment can yield additional benefits. Impurities which are retained with the metal in conventional processing tend here to escape from the molten titanium. Moreover, it should be possible to withdraw the product continuously in the form of a billet of substantial purity while the byproducts of the reaction escape as vapors. Thus, the additional purification steps which are necessary in the conventional process might be eliminated with a plasma process. Admittedly, in this program, materials of construction and particularly those involved with the containment of molten titanium, represent a difficult engineering challenge.

At the Homer Research Laboratories of Bethlehem Steel, a program for the direct plasma reduction of iron

ore is being carried out under the direction of Dr. D. R. Mac Rae.⁵ Operations have now been scaled up to the one megawatt level, and it has been reported that production of iron has been accomplished with a specific energy input of only 1.2 kWhr/lb. This figure is compared with 1.0 kWhr/lb from a theoretical thermodynamic standpoint. If correct, this kind of efficiency represents a new record in the achievements of plasma chemistry and augurs well for the future success of this ambitious program. In reporting on his work, Dr. Mac Rae continues to make a significant point which bears repeating. He recognizes that the plasma equipment employed in a process must be matched to that process according to the job which is to be done. In the light of the variety of types of equipment which are already being employed in the infancy of our industry, it seems highly unlikely that a single plasma torch design or even a single general type of torch will predominate as the industry progresses.

As might have been expected because of the increased cost of hydrocarbon feed stocks, new interest is being shown in the use of coal as a source of acetylene. The plasma route to acetylene from coal was already projected to be competitive with the conventional process before the large price increases took place. The conventional technology uses ethylene as the starting material, and its cost has increased several fold in the past 2 yr. Westinghouse has a great deal of confidence in the plasma route to acetylene from coal and plans to mount a substantial development effort in this direction soon. The company also anticipates commercial activity in the manufacture of pigment grade titanium dioxide. Here, as described by Dundas in 1970,⁶ a plasma heater would replace the quartz serpentine heat exchanger to elevate incoming gas temperature. A substantial amount of attention has also been given to this process by the Russian workers.

Without doubt, there are numerous other programs in large scale plasma chemistry in existence, some of which are close to commercial operation. Unfortunately for purposes of scientific information exchange, as noted above, some of the processes being worked on, for the very reason that they do have commercial significance, must be kept in secrecy during their development. Although this creates certain difficulties in our collective efforts to advance the state of knowledge, we should actually be pleased in terms of what this implies for industrial plasma chemistry. Surely, the existence of proprietary activities is a characteristic of a mature discipline and highly desirable from the standpoint of the future of our profession. To those of you in attendance here who are prevented by practical circumstances from discussing your work with us, we nevertheless say "Bienvenue". We wish you the best of luck in your endeavors and eagerly await the day when you will be able to share the details of your experiences and findings with us.

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