

R. B. Bennett

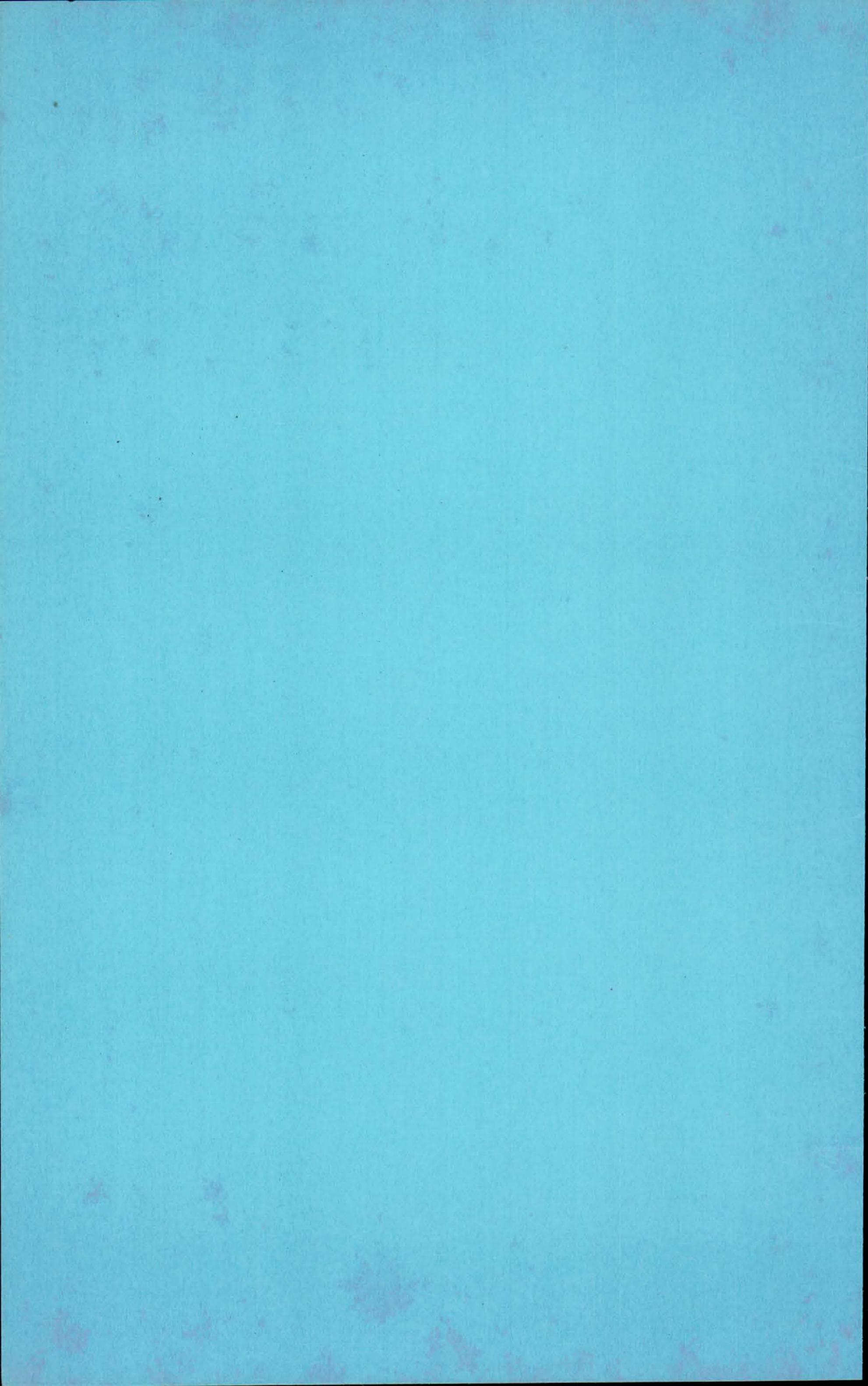
# CHEMICAL ENGINEERING EDUCATION



CHEMICAL ENGINEERING DIVISION

THE AMERICAN SOCIETY FOR ENGINEERING EDUCATION

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## MATERIALS AND CHEMICAL ENGINEERING

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Our materials of engineering have undergone a major technological evolution within the last five or ten years. Although the rapid strides have not involved the chemical engineer as extensively as it has engineers from other disciplines, the changes which have occurred are of interest to the chemical engineer because he is responsible for a number of the processing steps which are required in materials production. Furthermore, the chemical engineer has received new materials with which he may build his equipment and base his designs.

The topics of the next six papers will be concerned with the role of the chemical engineer in materials processing, the role of the materials engineer in the chemical processing industry, the considerations which must be given to materials in chemical process design calculations, and the significant problem of corrosion and its control through materials design and selection. Each of these will lead to the pedagogical problem of how do we teach the required topics to our chemical engineering students. Two approaches may be taken, viz. through physical chemistry and through engineering. Obviously the optimum approach is probably some combination of the two; however, we shall hear opinions on the contributions of the two academic areas.

### Materials Science

The rapid evolution which has occurred in the general area of materials during recent years is a result of two situations: (1) There has been a demand for improved materials for the more complicated designs of present engineering. Previously available materials have not met these demands. (2) Science has provided the engineer with a better understanding of the nature of materials as a consequence of advances in solid state physics and crystal chemistry. These advances have permitted general underlying principles to be formulated. These principles present a better means of extrapolating our knowledge for use with the development of new and improved materials. Simply stated, the basic underlying principle in the science of materials is "properties are controlled by the internal structure." Thus (1) if we know the internal structure of a material, we can be more specific about the material's properties, or (2) if the processing or service condition which are encountered by the material alter the internal structure, then we can anticipate a change in the accompanying properties.

The significance of structure on the properties and behavior of materials has changed the teaching and engineering considerations from previous descriptive approaches to approaches that take into consideration (1) the atomic structure, (2) the arrangement of atoms into molecular and crystal structure, (3) the arrangement of phases into microstructures, and (4) variation of microstructures within macrostructures. This systemization has permitted the establishment of principles which are usable with various types of materials whether they be metallic, ceramic, or polymeric. In general, the materials specialist is concerned with solid materials; however, the principles which are developed may also be used for liquids if appropriately applied.

### Materials Processing

In general, there are two types of processing which are encountered in the manufacture of any engineering material. These include (1) chemical processing, and (2) mechanical processing. In addition, consideration could be given thermal processing; however, thermal treatments are generally used to facilitate the chemical and mechanical processing through changes in the equilibrium, kinetics, or properties of the materials.

The chemical engineer has participated extensively in the processing of polymeric materials and less so in the processing of metallic and ceramic materials. If the chemical engineer is involved in the processing of materials, he must be fully conversant with the specialist who specifies properties and applications. Conversely, if the metallurgical or ceramic engineer is to have his full effect in the manufacture of materials, he must be cognizant of the processing principles which the chemical engineer and the mechanical engineer have developed.

#### The Materials Engineer

The materials engineer may bear the label of metallurgist, ceramist, or plastics engineer. In any case he is a specialist who is concerned with (1) the development of new materials, and (2) the critical application of materials in engineering design. As such he fills the gap between processing and engineering design. The materials engineer must understand the basic nature of materials so that he may develop real materials from the chemists' and physicists' ideas. Furthermore, he must understand the service conditions which prescribe the designed requirements. To this end he must be conversant with the mechanical, electrical, structural, and chemical engineer. The procedure for training men to fill this category is a subject of active discussion in many academic circles.

#### The Future

The engineering future as measured by the present research and development indicates that several areas will receive emphasis with respect to materials processing by chemical means. Foremost among these is the emphasis upon greater purity. This emphasis ranges from the beneficiation of existing raw materials so that they have more consistent and desirable composition, to the demand for extreme purity in the manufacture of many of the newer electronic and higher temperature materials. A second area of projected activity is into the processing of new materials with compositions and structures which have not been utilized heretofore on a commercial basis. Often this means high temperature or special pressure and catalytic requirements. A third area of future expansion is that of the production of single crystals. Currently we think of single crystals as laboratory specialties. The demands for single crystals have only been scratched and almost certainly the variety and tonnage requirements will be sufficient to build several special industries.

#### Summary

There has been a rapid evolution in the area of materials science and materials development. The chemical engineer along with engineers from several other disciplines are deeply involved. Furthermore, we should expect significant changes to occur in the foreseeable future.

## THE CHEMICAL ENGINEER AND MATERIALS PROCESSING

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Before getting on with subject given in the title, it is well to say something about engineers in general before dealing with the chemical engineers in particular.

Engineers deal with things and people as they are related to things. Granted an engineer deals with ideas also, but nowhere to the extent of say, a researcher. Things are difficult enough, but people are even more complex. Because of this large intermeshing with people the engineer becomes involved in broad non-technical generalizations which definitely deal with philosophy. Therefore, considerable of what I shall say will deal with philosophical aspects of an engineer's work, which are as important, in my mind, as the more commonly accepted technical aspects.

Frequently an engineer must listen carefully to the lowest man on the totem pole to get clues toward the solution of problems. At the other end of the spectrum he has to sell his solution to his superiors, who may or may not be technically trained. If his supervisors are technical by training his selling is perhaps a bit less difficult, but he still must sell his solution. In the latter instance of a technically trained superior, it is my experience that he thinks more as a manager than engineer per se, and this is as it should be. The engineer should realize that all his solutions will not be accepted, because upon comparison to many other things that management has on mind his solution is not important. Just because of this it can be helpful to be selective in choice of problems, both from the standpoint of relative importance to the whole endeavor, as well as to available resources. The question can be put to me "Were you always aware of this?" The answer is in the negative and it can be said that osmosis is a slow process. But then learning people is a slow process.

Having said something about an engineer in general we shall deal with our subject the chemical engineer. At first glance it is sound to say he has to do with engineering aspects of chemical manufacture, for example sulfuric acid. Most people would not consider titanium dioxide pigment manufacturing as a chemical business but it is just as much so as petro-chemicals. Thus, a chemical engineer is a person who in school has had much formal chemistry, more than other engineers, has quite a grasp for fluid heat flow and has a good knowledge of a wide variety of unit processes.

As an illustration of what has just been said I should like to mention a particular session on metallurgical education, held a number of years ago at a national AIME meeting. Some of the professors wanted suggestions how to improve or strengthen the teaching of process metallurgy. Dr. O. Ralston, at that time head of Metallurgy Branch of the Bureau of Mines, and now retired, gave an answer that did not sit well. He stated that after many years of experimenting he found that it is best to teach chemical engineers some metallurgy and turn them loose than to try to teach metallurgist (physical for most part) unit processes. At the mentioned meeting a number of persons, including myself, voiced the same opinion as Dr. Ralston.

The chemical engineer, like all engineers has problems to solve, without creating too many in the process. Before getting into the matter of problem solving it is desirable to again talk about people. First there is the matter of receptiveness. When collecting opinions of description of events it is important to remember that you may have to ask your question a number of times and in different ways. This is necessary so that the other person understands your question and repetition causes the other person to think more actively. This can be construed as a form of harassment and the approach should be used only in the most important cases. A second version of receptiveness is when an associate or subordinate is trying to come through. The first time around you may not take to the idea discussed. This can be a result of poor presentation by the other person or lack of attentiveness on your part. Repetition by the other party may at times bring out good ideas because of your improved attentiveness or because of a better presentation by the other party. The same reasoning applies to one's superiors.

In general problems are related with new processes for old or new products. Then we have trouble shooting or fire fighting. In between there may be very time consuming problems having to do with causes and corrective measures for product variations.

Before solutions are sought it is important to know what the problem is. I shall give examples later to show that at times a problem appears on the scene because of a lack of meeting of minds on a specification and details of testing procedures contained therein.

In school we are taught to study literature before embarking on solutions. I agree with this concept. Having established the nature of the problem one finds that people are pained by the notion that they should struggle with the other chap's work before starting active work themselves. This may shock those of you in teaching, however, this is par for engineers a few years out of school. The few that do search the literature before suggesting solutions overdo it at times. For example, since messrs. X and Y wrote an article or book they must be right in all they say, a form of author worship. If this were the case there would be less need for most research. The difficulty is that publications are too frequently read and too infrequently studied.

Assuming that the literature and other background information has been studied we turn to suggested solutions. A typical case is where A makes a suggestion and B knocks it down as unworkable. Does B feel that A's suggestion is technically unsound or uneconomical or both? One never knows unless one inquires. The best approach is to confine the first discussions to technical evaluation of suggestions and then to evaluate the many aspects. To carry both at the same time creates friction, and is often a waste of time.

In any discussion of solutions to a problem it is nice to recognize precedence, provided this does not lead to a continued status quo. At times there is much more than meets the eye about a process. This is particularly true for a minor product that has been made for years without much complaint from customers. The rub is when a customer wants a lot of the stuff, made to a spelled out specification and a much lower price. This involves some sort of changes. The particular case is difficult, in that the process is not well understood, in that Joe and Mike have made the stuff for years without the benefit of a written or up-to-date operating procedure. They know how to make it at present scale, the engineers do not know, but must know before they make scale-up changes. This takes us back to the process of careful interrogation. This must be done most carefully because Joe and Mike have their guards up. Did they do something wrong and are you trying to eliminate their jobs. Gentlemen, this is a real problem to my mind.

The solution that chemical engineers come out with can require considerable effort by supporting research people. Sometimes the projected effort can be made brief by reasoning. After discussion with the research group the projected process should be understood. If we now assume that we have a stack of reports answering most of your questions we can make calculations just as if we actually had the reports. On infrequent occasions this approach will show that the suggested solution does not have merit. It is important to mention that some people have a mental block unless they have reams of data.

If the solution involves purchase of new equipment that you have not had experience with and cannot benefit from the experience of acquaintances in other plants, put in large safety factors. Most equipment manufacturers are carried away by their enthusiasm. Therefore, literature per se is usually very troublesome. To narrow the gray area, telephone calls or visits and conferences are very much in order. I well recall the time we decided to replace an old and tired jaw crusher. Literature from seven manufacturers was studied. Many words were printed by all of them, but not a word about type of bearings or nature of jaws. Phone calls revealed that only one distributor could answer the critical question. One wonders, how as a nation we can compete with other countries if this example is not a rare one.

What one runs into in the processing field can best be illustrated by random examples that I have been exposed to. This does not mean that I have been directly associated with each experience, for some of them have been called to my attention by friends in other plants. A few examples are as follows:

a) A specification on a powdered material gave a distribution of particle sizes with a part being "not more than 15% thru a 325 mesh". The customer got 65% thru a 325 mesh screen which was difficult to understand in that we wet washed on this one sieve and he dry screened only. Exchange of samples used

for testing yielded the same results. There were letters and there were telephone calls and finally a meeting of four people - two from each side. After about a half a day it became clear that our super assumed assumption about ASTM standards were not valid. We assumed that the sample was re-tapped for 15 min. per standard, but no, the customer used 30 min. In any event, when both labs used either time they checked. What is grain size?

b) Again dealing with particle size and philosophy I remember well a case of milled rutile that was a bit finer than specified. Since it went into a weld rod coating we saw no harm and shipped the product. Customer rejected product. At first this appeared harsh. Finally it turned out he had a case. A rather dark substance like rutile will have a progressively lighter shade as particle size is reduced. The customer agreed that the welding characteristics would not be impaired but were uncertain about a welder in the field, who sometimes makes up his mind he has a different rod and he will manage to prove it does not work. So you are technically right, but are you going to suggest to a foreman in that field that he prove to the welder you are right?

c) Take the case of an operating procedure that stated "Pump A into tank M then pump B from tank N into tank M and heat to boil and agitate". In some instances this type of instruction may be valid, but in case of precipitation of hydrates it is not. The time to boil, and type of agitation must be spelled out. Again if you want the same results today as yesterday you had better make your instruction at least concise enough to have assurance that your desire is met. If you do this much you have an easier time of tracing trouble when it arises.

d) There is the case of a frit manufacturer who decided that it would be less expensive to have the vendor calcine borax ( $\text{Na}_2\text{B}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), since about half is water and save on freight. Then too it seemed to make sense since he would have to supply BTU's to remove water in his fritting furnace if the vendor did not. The dehydrated product did not produce good frit. After much to-do one lad woke up and realized that things were not the same as they had been. So dehydrated material was moistened with proper amount of water and satisfactory frit was produced. The assumption made was that at the frit making temperature, (say  $1300^\circ\text{C}$ ), the water could not be part of the melt. A very plausible notion but not a valid one.

e) Another example of the role of water in high temperature reactions is preparation of titanium diboride by reacting titanium dioxide, carbon and boric acid. At  $1600/1800^\circ\text{C}$  very nearly theoretical product is obtained. When anhydrous boron trioxide is used a very poor product is obtained.

f) A customer requested a fair quantity of a zirconium soap dissolved in mineral spirits. To do the job safely meant that operations had to be placed in an explosion proof building, etc. Since the quantity was not large the cost came out fairly high. Whereupon one staff member suggested we make a solid soap and let the customer dissolve it in solvent. This drastically reduced cost not only because a special building was not needed but also because a given size kettle can produce more pounds per hour. All of which demonstrate that requests are not unalterable, as we are lead to believe at times.

g) Zirconium metal, which by laboratory tests is superb in concentrated boiling hydrochloric acid, was made into a valve that failed after three weeks service at room temperature. In this instance reagent acid was used for laboratory testing while service was with commercial acid that had a few hundredths of a percent of sulfates and iron.

h) In another instance a product we make was off specification on small amounts of iron. After much discussion it became clear that despite changes our raw materials should be analyzed. It turned out that our supplier of hydrochloric acid was not adhering to the specification. This is a particularly knotty area in that cost is added in analysis of raw materials, yet you have to have a cross check even though the vendor is supposedly adhering to a specification.

In the process of closing this delivery I would like to add one final word of caution. This has to do with the biggest curse of all - the concept of an average - it should be outlawed in engineering certainly.

## THE MATERIALS ENGINEER IN THE CHEMICAL INDUSTRY

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The materials engineer should start evaluating possible constructional materials, to minimize capital investment, with the earliest decision to commercialize a process. This evaluation continues, with suitable modifications because of equipment and process changes, as the design develops. Specifications and procedures are drawn up so materials can be purchased and fabricated to give the results expected. Finally, plant operations are followed closely to assure that specified corrosion controls are maintained, that new controls are added or modifications made as needed, and that the materials used deteriorate in service only as predicted. With such a broad scope of activities, the materials engineer can function properly only if he is an integral part of the process team from inception to ultimate plant operation.

### Some Ground Rules

Two terms should be defined at once to minimize possible misunderstanding. First, the materials engineer discussed here is not trained in the field of "materials science" which is receiving so much attention and publicity from the government and from many of our colleges and universities. He is not supposed to develop new materials but is to utilize, most effectively and economically, existing materials that can be purchased and fabricated with definite schedules and lead times. The basic constructional materials still are metallic, so a good grounding in metals and alternate engineering materials, and the ways in which they can be modified and can deteriorate in service, is essential. However, even the best men trained academically in materials science will be of little direct value to the chemicals industry that needs a materials engineer.

Second, the term "chemical industry" means a plant which must operate at a satisfactory profit under a civilian economy in which urgency of plant completion is not necessarily the key factor and taxes are paid and capital investment is recovered without artificial incentives. The capital requirements and operating costs of a proposed plant are the major factors that determine whether or not it will be built. These costs, in turn, depend largely on the materials of construction. Therefore, the materials engineer, who has the responsibility for their choice, plays an important role in the commercialization of new processes or products.

### What Has To Be Considered

Consideration will be given, first, to the over-all picture and how the materials engineer should fit into it; second, to certain practical questions which must be answered, usually by Management; third, to the metallic and non-metallic materials available for use, either as constructional materials or as liners or coatings, with some of the limitations they impose; and fourth, to the information secured from the operating plant to control materials deterioration.

### The Over-All Picture

When a decision is made to build a new plant, the engineering and process designs usually have to be reasonably well fixed in order to estimate capital investment. The major factors affecting this investment, therefore, are materials selection and servicability. Service deterioration usually results from corrosion or some combination of it and another factor, such as mechanical wear, cyclic stressing (known as fatigue), or over stressing (leading to premature failure by cracking). When plant operation is at elevated pressures or temperatures, such deterioration is particularly hazardous because either the raw materials or the products, intermediate or final, frequently are flammable and may be noxious as well. It also can be costly because leakage or spillage may cause loss of valuable raw material or product while the plant is trying to operate. Even when there is no hazard or direct loss, a plant not operating because of an unplanned shutdown is not profitable.

The materials engineer must select and specify (a) materials of construction, (b) thermal or mechanical treatments, and (c) methods of fabrication to satisfy the process requirements. He also must have assurance that the materials supplied and the methods of fabrication used actually are as specified. After the plant is built he must be completely conversant with all service experience and field failures.

In many plants this work is done successfully by several different engineering groups with the materials engineer acting largely in a liaison and coordinating capacity. However, even to coordinate all of these functions, he must be part of the project team from the beginning. He should be conversant with bench scale developments and must be part of the development team during the pilot plant and process and engineering design stages. His responsibilities should be well recognized and his knowledge and experience be utilized to the utmost.

### Practical Questions

Before a materials engineer can function effectively, certain practical questions must be answered. These answers usually are given by company management on the basis of specific cases or alternatives presented to it.

First, how much contamination can be tolerated at various stages of the chosen process design? Both competitive products and the economic considerations incident to establishing or breaking into a market are involved. Contaminants introduced with raw materials usually are recognized but those resulting from corrosion or wear of mechanical or process equipment often are overlooked. These impurities, usually metallic, may deactivate existing catalysts or catalyze undesirable side reactions as well as contaminate or decrease the yield of the final product. Contaminants from corrosion also have improved the yield or quality (e.g. color) of the final product. This has been overlooked when the pilot plant group did not understand the nature of the corrosion fully. Also, in many processes, the build-up of corrosion products during the earlier stages or in recycle streams is ignored because care is taken to purify the product by distillation, crystallization, or extraction as a final step. These are some of the reasons why the pilot plant, if possible, should be built of the materials projected for the final plant design. If this is done, any materials weakness or disadvantages may be shown up early when they are correctable. To overdesign the pilot plant so no corrosion occurs merely postpones the day of decision or trouble.

Second, must the engineering design conform to the requirements of applicable construction codes? These Codes may be local, state or national like the ASME Boiler and Pressure Vessel Code or the ASA Code for Pressure Piping.

Third, where will the plant be built? This can affect materials selection because it determines the type of worker who will run the plant and may affect safety considerations as well. Labor may be a significant factor, especially in foreign or previously nonindustrialized areas. The ability to secure replacement materials readily when needed, also might occur in foreign locations and might have a profound effect.

Fourth, what are the economics of materials selection? Although the materials engineer should be knowledgeable in this respect, the basic decision often is made by company management as a general policy. A plant may be built of corrosion-resistant (usually more expensive) materials to decrease or eliminate product contamination and maintenance expense, at the cost of a larger capital investment. Alternatively, less costly (usually less corrosion resistant) materials can be used, at the cost of a larger operating expense, which is immediately deductible for tax purposes. All chemicals plants are designed to be shut down periodically for inspection and rehabilitation. The lost production is part of the cost of doing business. A materials failure frequently results in an unplanned shutdown or an extension of a planned shutdown. If so, the added cost of this loss of production, which is properly charged against the materials failure, frequently overbalances completely the savings resulting from using lower cost materials in the first place. The best course might appear to be to use the lowest cost material that will last indefinitely. However, from a materials engineering viewpoint two other factors should be considered.

(1) There always is a possibility of something unexpected happening to cause serious deterioration or failure in the supposedly superior materials. This is particularly true in a new process about which not too much is known.

(2) Proper attention must be paid to the time value of money. As a relatively simple example, if \$100 is borrowed today (even if it is borrowed from yourself) it must be repaid in, say, one year by a larger amount, for example \$115. Thus, for this simple example, \$100 today is worth \$115 after one year, or the present worth of the \$115 a year hence is \$100. This \$15 increase also is known as the earnings rate of the \$100. Therefore, money which is not spent today can be earning a return in some other investment until it does have to be spent. It may cost considerably more cash in the long run to make a large investment initially and to have low operating costs (i.e., to have no repairs) than to spend less capital money and repair at scheduled intervals.

Fifth, how will existing business practices affect materials selection? Currently, the capitalized cost of the original installation is depreciated over its life at a rate set by the Federal Government, whereas the costs of subsequent replacements, so long as they do not upgrade the equipment, are looked upon as repairs to help the equipment reach that life and are expensed, (i.e., are deductible, for tax purposes, in the year incurred), even though they last more than a year. Thus current laws on taxes and rates can influence materials selection profoundly. As an alternative to a high initial capital investment, annual operating expenses often can be increased much more than would be expected. If such replacements can be made during regularly scheduled shutdowns, only labor and materials need be charged against the replacement, but not the loss of production which usually is much larger. A treatment developed to assist in decisions involving long and short-life components is given

in the typical charts in Fig. 1. With these charts, if any three of the four variables: (1) earnings rate, (2) life of long-life alternative, (3) life of short-life alternative, and (4) ratio of the costs of the two alternatives, are known, the fourth can be read directly. Also, when the life of the second alternative is unknown, as usually is the case, the same charts can be used to determine what the life of this alternative will have to be in order to break even. For example, a given piece of equipment can be built either of carbon steel with a relatively high corrosion rate so it has an expected life of two years or of a low alloy steel which costs twice as much. If the desired earnings rate is 15%, the right-hand chart in Fig. 1 indicated that the low-alloy steel will have to last more than six years to be economical. However, if the earnings rate is 25%, the low-alloy steel would have to last considerably more than 15 years, on the same basis. Thus, unless there are overriding considerations such as safety or preventing contamination, it often is not economical to use a more expensive material even if it last forever.

#### MATERIALS AVAILABLE

##### Metallic Materials

Only alloys based on iron, nickel, copper, and aluminum find much use in the chemical industries. The properties of the other four basic engineering metals: magnesium, lead, tin, and zinc, and their alloys, usually are not suitable.

Relative costs and other pertinent data for some common industrial alloys used for process equipment because of their combination of strength and corrosion resistance are given in Table I. Carbon or low alloy steel is the preferred material, because of low cost and ease of fabrication into process equipment. Stainless steels, usually of the higher alloy austenitic types of which 18:8 (18% chromium, 8% nickel, remainder iron) is the best known, are most widely used of the higher alloyed iron. The simpler nickel alloys are used where necessary but are about as expensive as can be used in process units today and still leave a reasonable capital investment. The Hastelloys (complex alloys containing nickel and molybdenum with some iron, chromium, tungsten, etc.) cost much more than the simpler nickel alloys and usually can be justified only for special applications. A large number of alloys based on these engineering metals are available for use. Selection between them depends on the particular application and usually is determined by factors such as the strength, both static and dynamic, and corrosion resistance.

Producers of materials plan on potential consumers doing most of the development work, particularly when the potential sale of product is relatively small, as it usually is in the chemical industries. Also, chemical processes requiring materials for corrosion protection, if not completely new, often have been revised in such a way that previous experience is limited or of little value. The consumer must find out for himself, or with the aid of experienced engineering contractors or vessel fabricators what strength, ductility and resistance to service deterioration are needed and how materials with these properties can be assembled into operating equipment. Sometimes thermal conductivity and thermal expansion also may be important.

New developments, both in materials and in the methods of using them are being announced continually, but a high percentage of these announcements are premature from the viewpoint of the chemical engineer and the materials engineer trying to make an operating plant from a process design. These new materials are largely a direct outgrowth of the extreme temperature, strength, and other requirements of the nuclear missile and space programs, and the tremendous amounts of money being spent to develop materials. Some of these new metals were a little more than scientific curiosities not too long ago. Initially, such materials are produced in sufficient quantity to permit some of their properties to be determined and some times to have a limited special application. An effort then is made to extend their use in the hope that quantity production can be achieved at correspondingly lower prices. During this period, advertising, technical papers, personal visits and technical seminars are used to alert and arouse the interest of potential users so it is easy to be oversold by this convincing flood of information.

However, the use of these new metals develops slowly in either government-financed or business-financed industries, usually because they cost too much. Table I includes titanium, probably the best developed and lowest cost of these new metals. Its cost still is comparable with that of the Hastelloys, even on a volume basis. Consequently, titanium becomes competitive today, only where corrosion resistance is the main factor and strength is minor.

In Table II several of the newer exotic metals are compared with carbon steels. The comparison is based on the simplest commercial form, frequently a metal sponge, rather than on a fabricated shape. Next to titanium the best developed probably is tantalum, but it is so costly that its use can be justified only when nothing else is available. Furthermore, although practical methods suitable for fabricating vessels and other plant equipment from these metals may have been worked out, it usually has been only for simple constructions and

on a laboratory scale. All of them are extremely susceptible to contamination by such elements as oxygen and carbon and usually by nitrogen and hydrogen as well. Hence, the scale-up factor from laboratory or small-scale fabrication to full-size process reactors or distillation columns may be far more difficult than would be expected. The materials engineer must know these facts and the state of the art at any time because, if the need for an alloy is known far enough in advance, fabrication procedures suitable for a specific application can be developed. Many metal producers and fabricating companies are anxious to work with potential users if the demand is great enough or the potential user will pay the costs.

TABLE I

## TYPICAL METALLIC CONSTRUCTIONAL MATERIALS NOW BEING USED

	0.2% Offset Yield Strength 1000 psi	A.S.M.E. Allowable Stress 1000 psi	(Plate) Relative Cost	
			Per Unit Weight	Per Unit Volume
Carbon Steels	40-48	15	1	1
Aluminum Alloys	4-11	1.6-7.3	6-9	2-3
Stainless Steels	30-40	17.5-18.75	10-15	11-16
Nickel and Monel	15-40	10-19	21	24
Hastelloys	50-58	20	82-100	90-125
Titanium	40-65	12.5	125-225	75-135

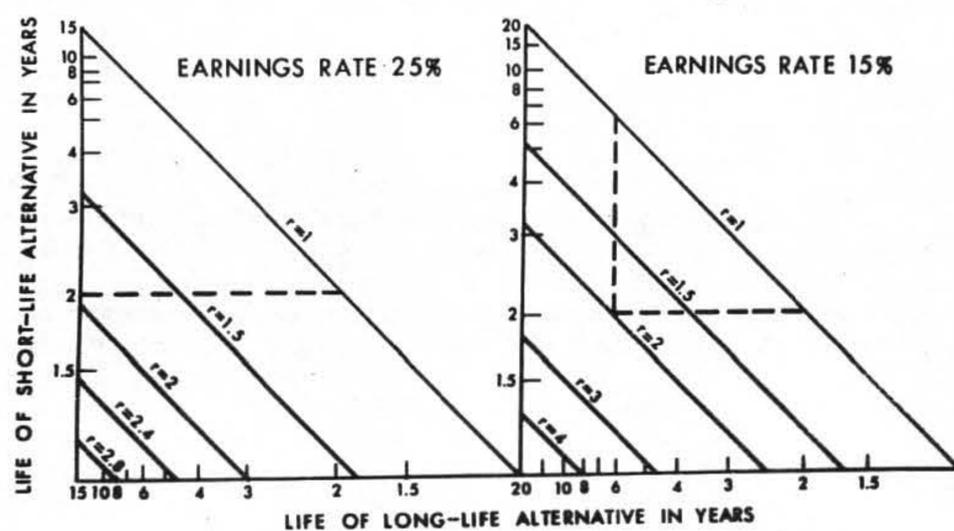
TABLE II

## PROMISING EXOTIC METALS

	0.2% Offset Yield Strength 1000 psi	Elastic Modulus $10^6$ psi	(Sponge) Relative Cost	
			Per Unit Weight	Per Unit Volume
Carbon Steels	40-48	30	1	1
Titanium	40-65	15.5	40-42	24-26
Zirconium	29-61	13.7	170	156
Molybdenum	70-80	47	210	290
Columbium	20-30	15	950-1450	1100-1700
Tantalum	30-40	27	920	2100

FIGURE 1

CHARTS FOR SELECTING BETWEEN A LONG-LIFE ALTERNATIVE AND A SHORT-LIFE ALTERNATIVE THE RATIO OF WHOSE COSTS IS  $r$ .



### Metallic Liners

Sometimes the more expensive corrosion resistant materials can be used as liners in process equipment. Many unexpected problems can arise with liners, however, especially in the initial application to a given process when elevated temperatures and elevated pressures are involved. Cyclic conditions are particularly troublesome. Leaks may develop which can be quite serious under operating conditions, particularly when the low cost backing material, e.g., carbon steel, has little corrosion resistance, and yet these leaks may not be detectable at the normal atmospheric conditions at which repairs would have to be made.

Three classes of metallic liners are in common use.

(1) Loose liners, either of the bladder type constructed externally for use inside a flanged steel vessel (which provides backing strength but not necessarily pressure tightness), or of the more conventional type constructed inside the vessel and supported primarily at the flange of each manway or nozzle.

(2) Welded liners, attached to the vessel either as fairly large panels using isolated or continuous spot welds or plug welds on a square or diamond pattern designed to take care of thermal expansion differences. Liners of this type also are made by continuous deposition of stringers of weld metal.

(3) Integrally-bonded liners, attached to the plates of which the vessel is made as completely as possible by roll welding, by casting and rolling, or by vacuum brazing.

With lined construction, however, savings on materials costs seldom exceed 25% and some of this saving may be used up by the special procedures required during vessel fabrication. For example, one factor which frequently is overlooked is that the clad plates themselves must be joined together to make the vessel and this may give considerable trouble. The welds joining these plates together generally have to be of carbon steel, but the process side either has to have corrosion-resistant weld metal, or be capped with a strip of corrosion-resistant metal.

### Nonmetallic Linings

Nonmetallic linings may be used successfully if materials serviceable under process conditions can be found. The carbon steel vessel itself may have adequate resistance to process corrosion if its temperature is low enough so the lining may only have to provide internal insulation to give a sufficiently low shell temperature at a low cost. The refractory concrete linings used to do this must be properly designed to avoid tensile stress-cracking and must have sufficient thickness of well-installed low-permeability material to provide good protection against corrosive fluids that might attack the shell but do not attack the concrete. Proper liner stress conditions seldom if ever can be obtained without decreasing the metal temperature substantially. Refractory linings intended primarily for corrosion control usually are made in one layer, supported by V- or T- studs. Two layer linings using lightweight insulating concrete against the shell and a thinner layer of dense concrete on the surface to resist erosion and corrosion are used frequently in vapor-state processes. In the two-layer lining, welding studs are used for support. If wear resistance is needed, hexagonal steel grating welded to these studs supports the dense concrete. Two-layer construction protects against corrosive vapors but is not reliable for liquid immersion. External insulation on the vessel must be eliminated or kept to a minimum if low shell temperatures are to result. Usually, shell temperatures are kept above the condensation range, however, to avoid both internal and external condensation corrosion.

Glass linings have been used in the past, within the limits imposed by their corrosion resistance and susceptibility to thermal shock and mechanical damage. In addition to the limitations obviously imposed by the training and habits of plant personnel, e.g., dropped wrenches or carelessly used hobnailed boots, glass linings can be used only with specially designed vessels. Modernized versions, partially crystallized borosilicate glasses (Pfaudler Company's "Nucerite" and Corning Glass Works' "Pyroceram" are examples. See J.R. Little and D.H. Hall, Crystallized Glass Coatings, Materials Protection, June 1962, 40-44) have greater resistance to both corrosion, thermal shock, and mechanical damage, and apparently higher temperature limits, than the older linings. They appear to hold considerable promise, but experience still is limited.

Likewise, the modern prestressed brick lining (C.A. Honigsberg and G.P. Eschenbrenner, Prestressed Nonmetallic Linings for Process Vessels -- Structural Design Considerations, presented at National A.I.Ch.E. Meeting, Los Angeles, California, Feb. 6, 1962; also J. Reys and A. Koepfel, Chemical Engineering Progress, June 1962, 92-94.), originally developed in Europe, appears to have definite advantages over the conventional acid-proof brick linings (Donald

Thompson, Brick-Lined Process Equipment, Chemical Engineering, Feb. 22, 1960, 129-134; March 21, 1960, 161-166). The prestressing is secured by use of an expanding thermostting organic resin or potassium silicate cement. This resin or cement is used both as a bedding material and as a mortar with either acid-resistant clay or carbon brick. Expansion of the mortar during a curing cycle imposes elastic compressive stresses on the liner. With proper design, these liner stresses are always elastic and are held within the compressive or, at worst, the very low tensile range, under all foreseeable conditions of operation. Each lining must be designed specifically for the vessel and for the process and other (e.g., cleaning and shutdown) conditions under which it must operate. Design is not difficult if operating conditions are nearly constant but it becomes much more complicated for cyclic conditions whether these are imposed by the normal operating cyclic or, for example, by steaming before shutdown.

The use of plastic coatings or linings for protecting steel vessels and piping against corrosion is growing. Usually these are applied best in the shop, preferably on new vessels or lines, rather than in the field because of the many cleaning and application problems involved in securing an adherent coating free of defects. If the surface already has corroded and must be cleaned thoroughly before coating, these problems are magnified greatly. Plastics for this purpose have definite temperature limitations. The older vinyl, epoxy, chlorinated rubbers and polyesters, and epoxy-modified phenolic coating materials seldom can be used above 220F. The newer chlorinated polyethers (e.g., Penton) after fusing at 425 F to 450 F, can be used to at least 250 F both as coatings and as solid components. The fluorinated polyolefins can be used to even higher temperature; FEP Teflon, for example, is usable to 400 F. However, the coatings are expensive (about \$8 to \$12 per sq ft as applied, 20 mil thick) and both application and service experience still are somewhat limited. Shop application of some of the new materials often is in the form of cemented sheet linings. However, for thermal plastic materials considerable progress has been made in plasma jet sprayed coatings on a developmental basis. The older TFE Teflon still has the highest potential service temperature (550F) of any plastic material but it is not thermal plastic so it cannot be sprayed or applied by fusion. Sheet linings of TFE Teflon can be applied by cementing with FEP Teflon but the cement then limits the useful temperature to, roughly, 400 F and the life of these linings still is somewhat questionable because of lack of service experience. The very high thermal expansion of Teflon (about 10 times that of steel) also may be a serious disadvantage. A successful solution to the TFE Teflon application problem would be a significant breakthrough.

Natural and synthetic rubber sheet linings are used widely at temperatures up to 200 F or slightly higher. They are not usually satisfactory in contact with organic solvents but provide reliable and durable protection against many aqueous solutions. Their cost is high compared to that of coatings, but sheet linings entail less risk of pinholes and have better resistance to mechanical damage and permeation by liquids than coatings. They are applied by using adhesives, almost always by specialists. Usual thicknesses are 3/16 to 1/4 in. Neoprene and soft or semiliquid natural rubber are used most commonly but nitrile and butyl rubbers and chlorosulfonated polyethylene (Hypalon) are better for some purposes.

Reinforced plastics, usually of the epoxy, or polyester types, also are much less used for linings or for primary constructional materials in chemical plants than might be expected from advertising literature. Both reinforced plastic pipe and plastic-lined pipe are finding increased usage, however. Acceptability by engineers and by plant operators has not been good if there is any other solution, and constructional Codes usually have not considered the question. Although reinforced plastics often have definite advantages over metals in corrosion resistance and light weight, they also may have definite disadvantages in low elastic modulus, which gives them poor resistance to internal pressure and to buckling and collapse, and in low flexural fatigue resistance, in poor flame resistance, and frequently in cost. Objection to the use of plastic piping has been particularly great if there is any possibility of fire. Resistance to overheating by fire is no more than a few minutes unless external fireproofing is used. However, service experience with reinforced plastic pipe, selected for corrosion resistance, generally has been good. Both cemented joints and flanged joints are used.

At the present time almost any vessels made of reinforced plastics have to be of standard shapes and sizes and usually have been used at substantially atmospheric pressures and temperatures. There are definite limitations regarding the number, size, and location of openings which can be used. For elevated pressures, proper reinforcement requires winding on specially prepared, relatively expensive mandrels which must be reused many times to be economical. For example, reinforced epoxy vessels have been made as large as 12 ft in diameter by 20 ft long, with a capacity of 17,000 gal. Even with a 1/8 in. wall thickness these tanks are more expensive than steel. In addition, because of the poor flexural fatigue strength of the reinforced plastic, a factor of safety of 6 to 8 must be used, as compared to 4 for steel, so a vessel of this size for 200 psi service would have to be 1 in. thick, about the same as steel without the corrosion allowance. Service would be limited to 200 F. The unfabricated materials cost of the plastic vessel would be about three times that of a carbon steel vessel; the fabricated cost much more.

Repair and Maintenance

The use of new materials in the chemicals industries is much freer when maintenance and repair are involved than for new construction. In these cases the requirements of the various constructional Codes either do not apply or apply less stringently than to new construction so the ingenuity of the engineers involved govern more than any arbitrary rules.

For example, although there are many objections to the use of glass-reinforced plastics as basic constructional materials, they are finding application for replacement and repair within the limitations of their chemical and thermal stability. For repairing a storage tank bottom (J.F. Wygant, Reinforced Plastic Replacement Tank Bottoms, A.S.M.E., Petroleum Division, Dallas Meeting, 1962.), for example, where the deteriorated steel can be used as a construction form, a glass-reinforced isophthalic polyester plastic bottom costs about half as much as a replacement steel bottom. Isopolyesters adhere well to sand-blasted steel and are appreciably less expensive and more adherent than the epoxies which also have been used.

CONTROL OF MATERIALS DETERIORATIONElectrochemical Control

Two methods of protecting metal vessels are electrochemical in nature. The first of these is cathodic protection, Fig. 2. In this method another material is made anodic with reference to the material being protected. The anodic material may be more active electrochemically and thus corrode instead of the metal being protected or it may be relatively inactive chemically and be made anodic by use of an impressed external voltage.

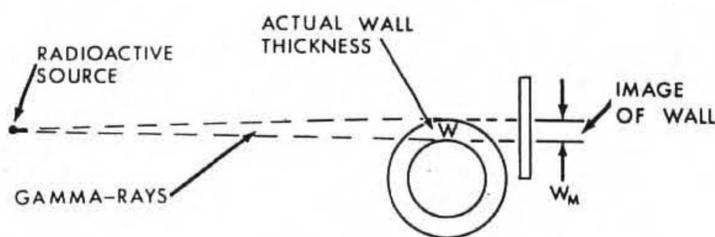
The second method is just the reverse, namely, anodic protection (C. Edeleanu, Anodic Protection, Chemistry and Industry, March 11, 1961, 301-308), Fig. 3. Many metals are resistant to corrosion in certain media because of the formation of a passive layer on their surface. For example, stainless steels have excellent corrosion resistance in the presence of oxidizing agents such as sodium dichromate or nitric acid but corrode rapidly in the presence of reducing environments. This corrosion resistance is a type of passivity, and, in stainless steels at least, probably results from the formation of a continuous oxide layer or monomolecular layer of oxygen on the surface. Passivity can be induced and maintained by keeping the metal anodic in the corrosion system, although this may sound paradoxical because, as mentioned above, the anode usually is the corroding electrode in such a system. In this new system of anodic protection the anodic potential must be kept under proper control so the metal remains passive. If it becomes active, it will corrode. Some sort of stable reference electrode must be used in the system, along with a cathode. The necessary relationship between electrode potential and log current or current density (proportional to corrosion rate) on the metal being protected is shown in Fig. 4.

In systems to which anodic protection is applicable (D.A. Shock, O.L. Riggs and J.D. Sudbury, Application of Anodic Protection in the Chemical Industry, Corrosion, 16, February 1960, 55t-58t.), as the potential first increases to a maximum (at point B). With a further increase in potential the current density decreases to point A and then remains substantially constant over a fairly wide range before it starts to increase again. This minimum-current range is the passive range. In it the current density is a minimum so the corrosion rate is a minimum.

Inspection Control

In many cases, the first real test of constructional materials under actual operating conditions comes only when the new plant goes on stream. Pilot plants often are used largely to outline feasible operating ranges. The optimum operating conditions then are determined by mathematical analyses. Even

FIGURE 9  
DETERMINATION OF PIPE-WALL  
THICKNESS BY RADIOGRAPHY—SCHEMATIC



if pilot plant runs are made under the expected full-scale plant conditions the scale-up to a full-size unit frequently introduced unanticipated variables which affect materials deterioration. Such things as localized process conditions or velocity effects, or differences in material characteristics resulting from construction techniques often cannot be predicted from either the process design or the pilot plant studies. Also, plant maintenance practices may introduce new corrosive conditions such as washing procedures or the formation of corrosive solid deposits or condensates in piping.

Four general procedures are available to give the materials engineer information on the service durability of the materials selected. Two of these: corrosion coupons and off-stream inspection, have been used for many years, but the other two: corrosion probes and on-stream inspection, are relatively recent developments. In addition, considerable insight often is needed to know where to look for possible deterioration in the time available. Any corrosion evaluation device is, in a sense, only a statistical tool because it can give information only on what is happening at a particular location.

In exposing corrosion coupons of various materials to operating conditions, the only real problems are the selection of materials and of a representative exposure location. Coupons customarily are evaluated by a combination of weight-loss measurements and visual and metallographic examination. They usually are assembled on racks, which are either bolted or welded to the vessel in the location selected. For liquid or condensation conditions, especially aqueous, some sort of insulators, e.g., Teflon, customarily are used to prevent electrical connection and eliminate possible galvanic effects. Selection of test specimens depends largely on the application but these specimens should be in a condition, e.g., welded or stressed, comparable to their use in the process equipment. Specimen thicknesses of the order of 0.1 to 0.3 in. frequently are used for mechanical durability, so long exposures are desirable to secure accurately measurable weight losses. Exposures usually are determined by the length of run between unit turnarounds. However, coupon changers now are available, which permit a limited number of coupons to be inserted or recovered during a run, even with pressurized systems. The chief disadvantage of coupons is that only average corrosion rates can be secured from them and even these require certain assumptions, of which the simplest and most commonly used is that corrosion occurs at a uniform rate. The main advantage of coupons is that they evaluate corrosion over a sizable period of time as well as giving some information on pitting or other localized attack.

Off-stream inspection (A.J. Freedman, A. Dravnieks and B. Ostrofsky, Corrosion Measurement Short Course, Petroleum Refiner, May, June, July, 1960.) largely consists of visual inspection and thickness measurements of any parts of the plant that are opened during the shutdown. This seldom includes all vessels, so, if there is no past experience record, locations of important materials deterioration may not be inspected. The likelihood of this is minimized if the materials engineer is part of the inspection team, if only on a consulting basis.

The corrosion probe (A.J. Freedman, E.S. Troscinski and A. Dravnieks, An Electrical Resistance Method of Corrosion Monitoring in Refinery Equipment, Corrosion, 14, April 1958, 175t), uses a very thin strip, wire, or tube specimen and evaluates corrosion rates by a series of measurements of electrical resistance (proportional to the loss in thickness). The slope of the

FIGURE 2  
CATHODIC PROTECTION SCHEMATIC

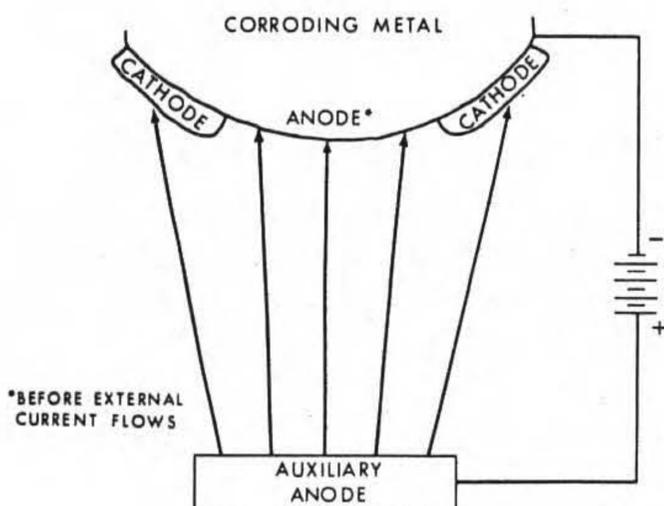
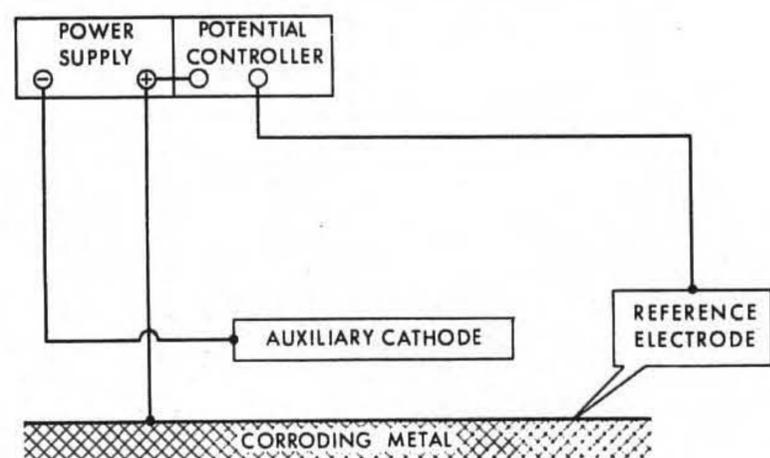


FIGURE 3  
ANODIC PROTECTION-SCHEMATIC



thickness-time plot then gives a corrosion rate, Fig. 8. The specimen is always in a selected location in the corroding medium so little if any information can be secured on localized corrosion such as pitting, etc. Probes are available which can be removed or inserted while the unit is in operation. Mechanical devices have been developed for doing this easily and safely at relatively high pressures. When inhibitor or other injections are being used to control corrosion, probes will give a continuous record of effectiveness. They also may be useful as operating tools to evaluate the effect on corrosion of changing operating conditions.

On-stream inspection now is being used more and more extensively, even at elevated temperatures. This has been a logical development. What a unit operator really wants to know is how much corrosion allowance is left at any time. This information should be available far enough in advance of a scheduled shutdown to have everything in readiness for immediate repair. In that way down time is minimized, sometimes enabling more expensive and longer life materials to be used effectively. On-stream measurements give the actual thickness of the material at one spot and can be made rapidly enough to permit numerous readings. Radiography (X-ray or isotope) and pulse-echo ultrasonic are now the most common methods of doing this. Radiography (L.A. White and T. Arnesen, Radiographic Techniques as Applied to Onstream Inspection Methods, Proceedings, American Petroleum Institute -- III Refining, 40, 1960, 190-195.) is effective only where the source and film can be placed on opposite sides of the part being inspected, Fig. 9. This usually means only piping or small vessels. Pulse-echo ultrasonic thickness measurements can be used whenever there is access to the spot to be measured. This presents no problem if the line is below, roughly, 100 F. At high temperatures, up to at least 1000 F, specially sealed and watercooled transducers must be used (B. Ostrofsky and C.B. Parrish, Ultrasonic inspection at Elevated Temperature, Society for Nondestructive Testing, New York Meeting, November, 1962.) Lead metaniobate crystals are satisfactory if protected properly. The cooling water also serves as a couplant thus simplifying or eliminating any requirement for surface preparation. Experience with on-stream inspection still is somewhat limited but it has proven to be strikingly effective in some instances by detecting severe and unexpected corrosion which undoubtedly would have resulted in a serious failure if the unit had continued on stream.

Any engineering design, whether for a chemicals plant on the ground or a rocket engine, is only useful to the extent that it can be translated into reality by using available materials. The selection of materials often does not seem to be complicated. However, this discussion may serve to emphasize the breadth of the problem and the large number of factors which must be considered if capital investment is to be kept to a minimum without paying for it by having a low operating factor. It usually is unanticipated equipment and materials problems that make a chemicals process unsuccessful.

FIGURE 4  
PLOT OF ELECTRODE POTENTIAL AGAINST CORROSION RATE TO ILLUSTRATE PRINCIPLE OF ANODIC PROTECTION

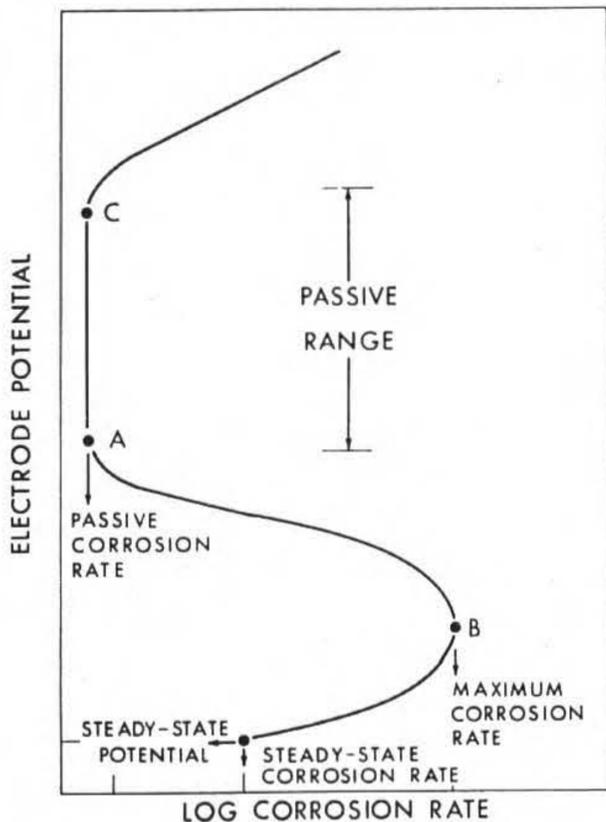
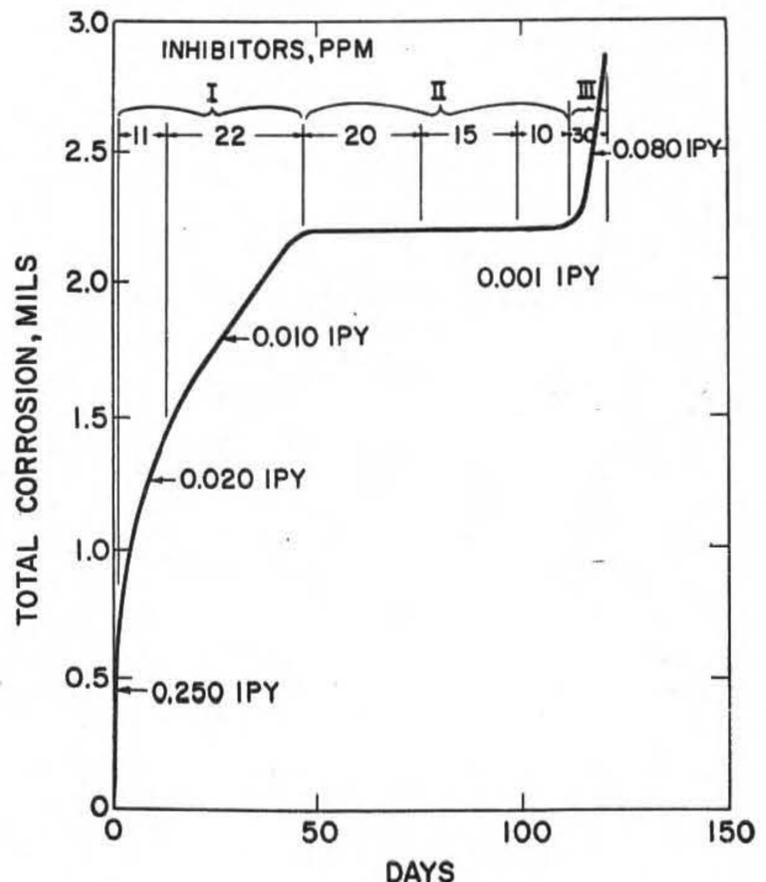


FIGURE 8  
TYPICAL PLOT OF CORROSION-PROBE DATA SHOWING VARIATION IN CORROSION RATE WITH TYPE AND CONCENTRATION OF INHIBITOR



## MATERIALS AND PROCESS DESIGN CALCULATIONS

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As implied by the title, the scope of this presentation could easily encompass such a vast range of topics it would seem discreet not to proceed any further and to state simply that in all process designs the best materials of construction should be used, consistent with sound engineering economics. To avoid speaking in such broad generalities it is expedient to concentrate on a specific design problem since the principles illustrated are applicable in a variety of situations.

Historically, chemical engineers have been primarily concerned in process design with the specification of materials for high temperature and/or corrosive service. Once a list of materials which will satisfy these service requirements has been prepared, it is then necessary to narrow the selection to materials which can accommodate the stress levels to be encountered in actual operation. The final choice of a particular material will then be dictated by purely economic factors which are measured in terms of life expectancy versus installation and maintenance costs. The use of the singular term, material, does not preclude combinations such as protective coatings, linings, and cladding which become evident during the cost analysis.

The increasing trend toward higher and higher pressures in commercial operation has pushed requirements beyond the metallurgical limit of available materials of construction as measured by conventional design standard and code. For the most part designers are guided by certain rules which limit working stresses to  $\frac{1}{4}$  of the ultimate tensile strength, the stress to produce a creep rate of less than one-tenth of a per cent in 10,000 hours, 60 per cent of the creep to rupture stress at 100,000 hours, etc. Fortunately, with improved techniques for producing materials, particularly in quality control, these design limits or factors of safety are gradually being relaxed.

In addition our increased understanding of the behavior -- most important the reliability -- of materials and our greater ability to predict theoretically stress levels at all points in complex configurations (attributed to the advent of digital and analog computers) has atoned somewhat our inability to invent exotic, yet economical, materials as new service requirements arise. Designers have learned to live with the shortcomings of the properties of materials by suitable provisions in design details; in some instances advantage can even be taken of these peculiar characteristics. For example, industry was plagued for many years by the unpredictable failure of boiler and furnace tubes. The tendency had been to make these tubes of sufficient wall thickness to eliminate creep at the expense of aggravating localized thermal stresses. Tube failures involved not only their cost of replacement, but also repair of damage to the furnace itself. By striking a compromise between the creep rate and thermal stresses, and by making periodic visual observations of the tube deformations, it is now possible to predict when the tubes should be taken out of service short of imminent failure. In this case, empirical laboratory data on creep and rupture life have been invaluable.

Another illustration can be drawn from Air Force experience. Technical regulations called for the replacement of a rubber O-ring in a critical component of a hydraulic system in a jet-bomber after so many hours of flying service. The concern here was not simply one of replacing an O-ring valued at less than 50-cents, but rather the cost of gaining access to the O-ring by dismantling the hydraulic system. The total direct replacement costs were estimated at over 700 dollars, not including the cost of bringing the aircraft to a maintenance base from some remote point or the cost of maintaining additional aircraft to compensate for such down-time so as not to weaken our military defenses. To make matters even worse, the O-ring was invariably replaced by one that had been sitting in a storage bin for several months during which it had deteriorated more than the O-ring in actual service. The solution to this problem is rather obvious, and is as simple as packaging a gumdrop, but apparently not convincing enough to penetrate bureaucratic red-tape as yet.

Chemical engineers are accustomed to service conditions which diminish the properties of the materials. For example, metals have less strength at high temperatures than at moderate temperatures. Within the last decade, chemical engineers have become involved in large scale operations at very low temperatures, and in so doing, have become confronted with a host of new problems in materials. Although it is well-known that, in general, all materials improve in strength with decreasing temperatures, it does not follow that material problems are necessarily lessened. In fact, at the present time advantage can not be taken of any improvement in properties with temperature simply because regulatory codes won't allow it.

In order to illustrate the physical and economic variables that must be considered in specifying materials for cryogenic service, the transportation of liquefied natural gas at minus 250 degrees Fahrenheit and at atmospheric pressure by ocean-going tankers will be reviewed. In the presentation that follows it is to be understood that it will not be possible to cover all aspects in detail. Consequently sweeping generalizations, conclusions, and extrapolations of the information presented herein would not be prudent.

Suppose you are confronted with the problem of fitting a tanker in the 20,000-ton class with the special equipment needed to load, contain, and discharge a cargo of 170,000 barrels of liquefied natural gas (equivalent to 500-million standard cubic feet of gas). The naval architect has specified the general arrangements for a conventional tanker with the exception of the tank storage compartments and auxiliary piping, fittings, and instrumentation for handling the liquefied natural gas. You also note that he has provided dual-fuel steam boilers for propulsion so that the boil-off vapors from the storage tanks during transit can be fed to the boilers if economical.

### Selection of Material for Tanks

The first step in the design is to determine the shape of the storage containers. At first it would appear that these tanks should be cylindrical to minimize cost of fabrication. But, is the fabrication cost of the tank the only economic factor to be considered in this instance? The cross-section of the hull of the ship is essentially square, and the plan view is rectangular as shown in Figure 1.

It is evident from Figure 2 that cylindrical tanks can utilize only  $\pi/4$  or less than 80 per cent of the cargo-carrying space. An analysis of the cost of the ship, operating costs, and value of the cargo reveals that the entire project is unattractive if even 10 per cent, much less 20 per cent, of the space is not utilized. Preliminary estimates indicate, however, that if the storage tanks are shaped to conform to the cargo space, prismatic or rectangular parallelepipeds, the project might be salvaged depending on what the installed costs of the tanks finally are.

The design of these tanks is unconventional for the chemical engineer because in addition to the static hydrostatic pressure loads, provision must be made for:

- (1) Stresses caused by cyclical dynamic loads due to rolling, pitching, and heaving of the ship.
- (2) Stresses caused by key forces restraining the tank's movements relative to the ship.
- (3) Stresses caused by thermal gradients, particularly the sharp vertical temperature profiles in a tank that is only partially filled.

Other factors such as maximum permissible deflections and overall and local instability (buckling of tank walls) must be considered.

The next step is to establish the general size of the tanks in order to make maximum use of the cargo space. Obviously, one large tank filling the entire cargo space would be cheaper than several smaller ones. However, the size of any one tank will be limited by two factors:

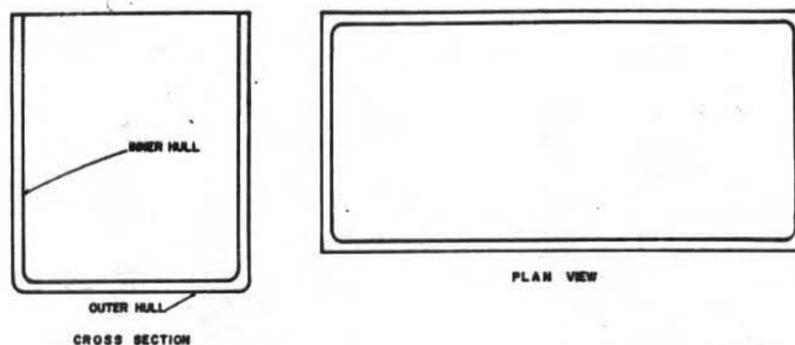


FIGURE 1: SHAPE OF TANK HULL

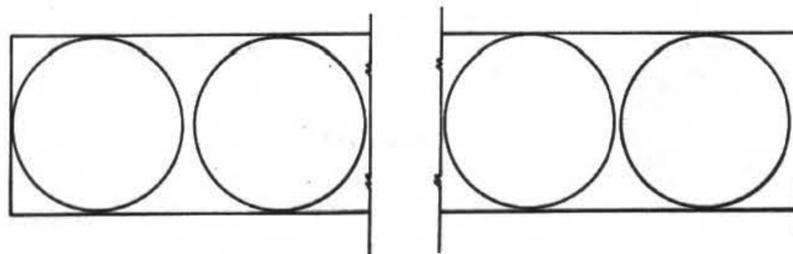


FIGURE 2: LOSS OF CARGO CAPACITY BY CYLINDRICAL TANKS

- (1) Regulatory bodies for ships have established limits for individual compartments subjected to dynamic loadings, free-surface liquid effects, and safety under collision conditions.
- (2) The maximum capacity of equipment to lift a completely fabricated tank (on the dock) approximately 75-100 feet into the ship's hold. (Alternatives would include assembly of tank in situ or installation during early stages of ship construction.)

Once the overall dimensions of each tank are established, shown schematically in Figure 3, design details such as sizes of plates and stiffeners must be determined. To do so requires a knowledge of the stresses which in turn are dependent on the elastic modulus of the material of construction. Therefore, the next step is to select the material.

It is common knowledge that materials having a body-centered cubic lattice generally tend to become brittle at low temperatures, whereas face-centered cubics or hexagonal close-packed do not. In this connection laboratory tests such as the Charpy impact at various temperatures, which is qualitatively represented in Figure 4, are useful. It will be noted that around zero degrees, carbon steel shows a sharp drop in impact energy denoting a transition from ductile to brittle behavior. Nine per cent nickel steel shows a more gradual transition whereas stainless steel and aluminum alloy show no transition at all. The absolute values of the impact energy have no known theoretical significance although as a rule of thumb in design practice, values of impact energy of at least 10 to 15 foot pounds are considered minimal. Aluminum alloys have a value of about 30 foot pounds or roughly  $\frac{1}{2}$  of the value for stainless steel. Nine per cent nickel steel, although tapering off at low temperatures, is considered suitable down to about  $-320^{\circ}\text{F}$  (liquid nitrogen). Care must be taken in drawing final conclusions from Figure 4 for any materials which undergo a transition. Considerable variations can occur for the same material from different heats; data in the literature on carbon steel for example indicate transition temperatures that vary as much as between minus 200 and plus  $200^{\circ}\text{F}$ . Furthermore, the ductile to brittle transition temperature can be some 200 degrees lower for uniaxial loading as compared to triaxial loading; the source of the data is therefore important to know.

From Figure 4, three candidates for possible materials of construction emerge. Since stainless steel costs about 60 per cent more than aluminum it is tentatively eliminated (copper and copper-based alloys are suitable for low temperatures, but their costs rule them out for large-scale tanks). Nine per cent nickel steel has an allowable design stress of approximately twice that of aluminum alloy; however, since the tank walls are flat plates rather than cylindrical, the advantage gained by nickel steel is only the square root of 2 or 1.4 (stresswise) over aluminum alloy. On the other hand nickel steel has a density of about 2.8 times that of aluminum. Therefore, the cost of the nickel steel will have to be somewhat less than the aluminum to be competitive for this application.

Consideration must next be given to other properties which might influence the final design and material selection. Figure 5 shows that the tensile or yield strength of all materials of construction increases with decreasing temperature. For metals this increase amounts to a factor of 1.5-2.5 between ambient and liquid nitrogen temperatures, whereas for plastics (Mylar, polyvinyl chloride, Teflon) it varies between 1.5-7.0.

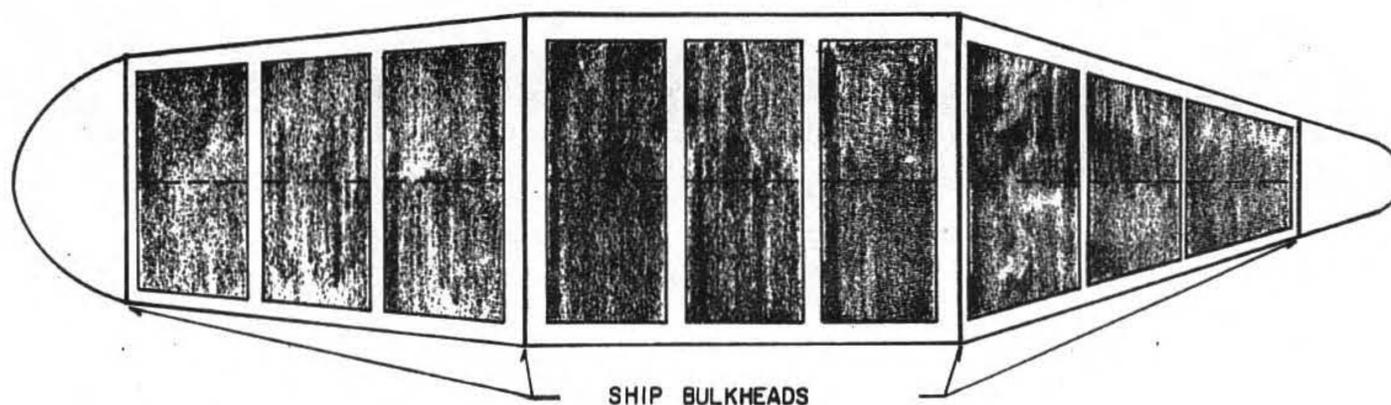


FIGURE 3: PLACEMENT OF PRISMATICAL TANKS IN SHIP'S HOLDS.

The elongation, like the impact value, gives a convenient, qualitative indication of the degree of ductility. There does not appear to be any way of incorporating numerical values of ductility into design equations any more than impact values. However, the greater the ductility the less tendency there is for build-up of stress concentrations. Theoretically, a ductility of only 2-3 per cent is more than adequate to relieve localized stresses; nevertheless experienced designers prefer not to work with materials having an elongation less than 10 to 15 per cent in general construction.

The cargo tanks will be subjected to cyclical loadings due to motion of the ship and vibrations. Fatigue life is thus another important variable. The stress to cause fatigue in a million cycles increases from about 1 to 3 times as the temperature is decreased from ambient to minus 300°F. Specifically in the case of aluminum alloys this improvement is about 1.4.

The next question that arises is whether any of the properties or combinations thereof will influence the design. The thermal stresses that can be developed in a bar of material with the ends fully restrained during cooling is given by

$$s = \alpha E(\Delta T)$$

where  $s$  = stress  
 $\alpha$  = thermal coefficient of contraction  
 $E$  = modulus of elasticity  
 $(\Delta T)$  = difference in temperature

If the yield stress of the material is not to be exceeded then the ratio  $s_{yp}/\alpha E(\Delta T)$  will determine whether the fully restrained specimen will yield inelastically. If the ratio is less than one, then provision must be made in the design to permit sufficient freedom of movement so that the yield stress will not be exceeded. If the ratio is greater than one, then the material will not yield even if fully restrained. In the case of the tank, which is only keyed to the ship's structure and not rigidly attached, this ratio criterion is not particularly important since the tank is essentially free to contract in all directions. However, as will be clarified later, this ratio criterion is significant in selecting the insulation for the tank.

Actually the ratios should be computed for the two-dimensional model (plate) rather than the one-dimensional (bar) to include the Poisson ratio effect. On this basis the values reported above would be reduced roughly 10 per cent for the metals.

It is interesting to compare values of this ratio for several common materials:

<u>Material</u>	<u><math>s_{yp}/\alpha E(\Delta T)</math></u>
Wood	2.2 - 9.2
Cast iron	2.3
9% Nickel steel	1.2
Foamglas	0.45
Concrete	0.3
Stainless steel (304 annealed)	0.28
Aluminum alloy (5000 series, annealed)	0.22

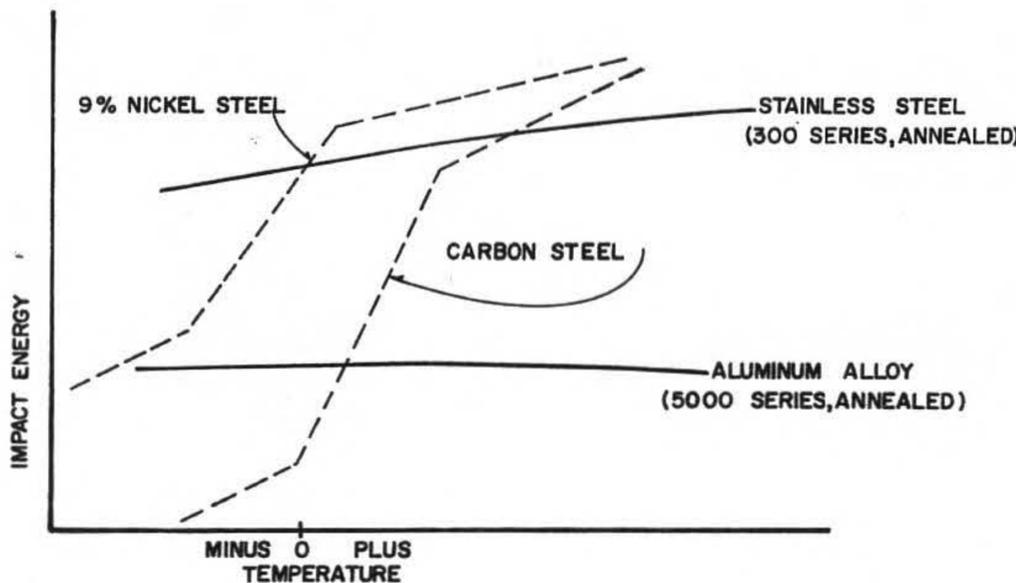


FIGURE 4: IMPACT STRENGTH OF VARIOUS METALS, EFFECT OF TEMPERATURE

The above values are computed on the basis of properties measured at ambient temperature and  $(\Delta T)$  is taken as  $(60 + 320)$  or  $380^\circ\text{F}$  for service at liquid nitrogen temperatures. According to the table, the only metal that can withstand liquid nitrogen temperatures when fully restrained is 9% nickel steel and cast iron. Cast iron of course is ruled-out for cryogenic service because of its exceedingly brittle nature. On the basis of this ratio criterion, wood is the "strongest" material of construction known for cryogenic service.

The ratios given above are conservative. Since  $\alpha$  decreases with decreasing temperature and  $E$  increases (about 10 to 15 per cent) with decreasing temperature, these two variables tend to counterbalance each other. The yield point as noted in Figure 5 will increase by a factor of 1.5 to 2.0. Therefore, the ratios will be greater at lower temperatures than those reported above.

So far the properties examined and the conclusions reached were based on data in the unwelded condition. It is important before a final selection of material is made, that information is obtained on the welded condition since the properties in the heat affected zone will be limiting. If the material to be used is initially in the annealed condition, then the properties of the welds will not differ significantly from the properties of the parent metal providing quality control and specifications for the welds are rigidly observed.

### Stress Analysis of Tanks

In any project for which the economics are fairly tight, there is no room for sloppy or ultra-conservative design. Since the ship's tanks constitute not only the critical part of the entire design, but also a major cost item, they will have to be optimized to the highest, possible degree. Two problems must be faced. First the tank configuration and details must be established to carry the dynamic, mechanical loadings. This particular design must then be checked for thermal stresses. If these are not satisfactory, the mechanical design must be modified and the entire process of analysis repeated.

Preliminary calculations reveal that:

- (1) The tanks must be braced at the corners with diagonal struts. Depending on the reinforcement achieved, additional tie rods extending across the tank may have to be used.
- (2) In order to avoid excessive plate thickness, the tank walls will have to be stiffened. These members will have to be attached in successive horizontal planes which are spaced at variable distances apart, decreasing in spacing with depth in the tank. (The other alternative would be to use a constant spacing between the stiffeners and to vary the plate thickness with depth). Stiffeners running in the vertical direction aggravate the thermal stress problem and therefore are not considered further.

With these limitations, surprisingly few alternative designs are permissible. Of the several possible, the one shown in Figure 7 appears most promising. The most severe loading condition will occur at the point of maximum roll of the ship. It can be seen from the loading diagram in Figure 8 that the ship is "tipped" to the right. This loading condition will be reversed every ten seconds. The design point will then be the condition of maximum roll and should be such that stresses in the tank members are at or near the allowable design value. To achieve this idealized result, a digital computer analysis is mandatory.

The next step is to incorporate certain assumptions which will make the stress analysis more tractable but at the same time will yield realistic re-

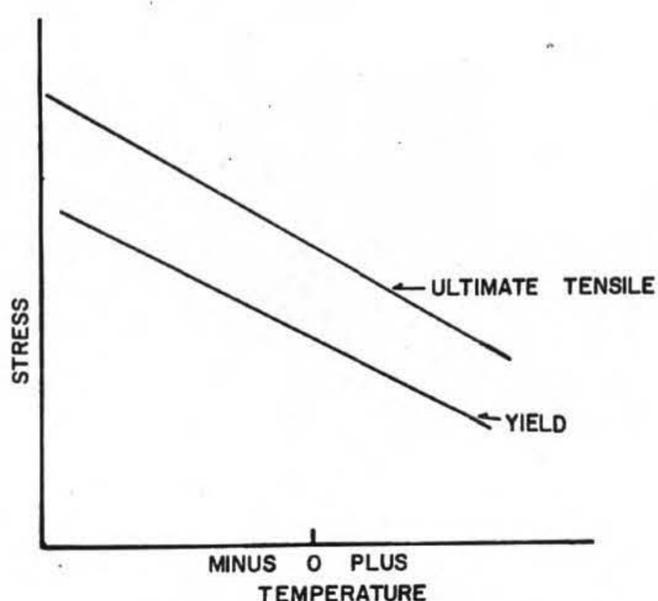


FIGURE 5: EFFECT OF TEMPERATURE ON

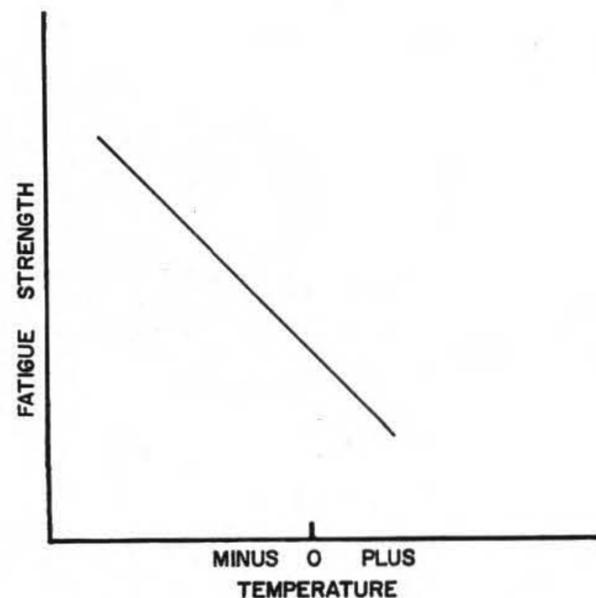


FIGURE 6: EFFECT OF TEMPERATURE

sults. By assuming that the load-carrying capacity of the tank walls is represented by a system of statically equivalent beams, the tank may be interpreted as a three-dimensional truss consisting of a finite number of rigidly connected bars. This approach would yield a rather precise solution via a "transfer-matrix" procedure, but the cost of computer time would be unreasonable. The problem, can however, be simplified without serious loss in precision into a two-dimensional one by assuming that the pressure loads are carried by a series of mutually, independent, horizontal slices of the tank. The simultaneous solution of the differential equations representing the pressure loads and the subsequent matching of the boundary conditions is carried-out numerically on a digital computer by means of a "stiffness-matrix" method of analysis.

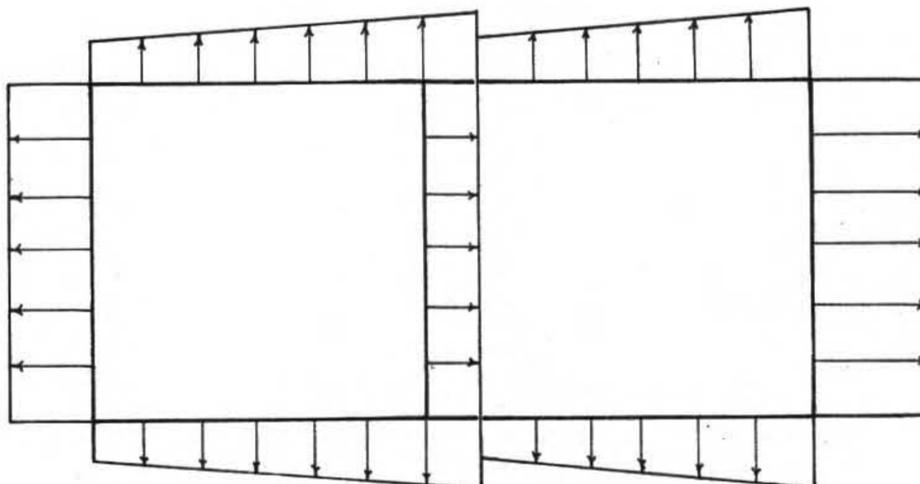


FIGURE 8: RESULTANT LOADING DIAGRAM (STATIC PLUS DYNAMIC)  
ON VERTICAL TANK WALLS.

The final step is to check this design for thermal stresses. From a knowledge of the heat leak the vertical temperature gradients, and therefore the thermal stresses, can be determined from a numerical solution of the differential equations involved with the aid of a digital computer. The most severe thermal stresses occur when the tank is nearly empty at which time the hydrostatic stresses are a minimum. Therefore, it is only necessary to establish that the thermal stresses do not exceed the allowable design stress.

The thermal stresses will be dependent on the material of construction. In this case, aluminum alloys show lower thermal stresses than stainless steel or 9 per cent nickel, although in the latter cases excessive stresses can be avoided by designing around them.

Before the final selection of the material, consideration must be given to the feasibility of maintaining quality control on the welds:

- (1) Stainless steel is the most desirable from the standpoint of ease of welding and 100 per cent X-Ray is not mandatory although it is desirable.
- (2) Aluminum alloy welding requires special precautions against excessive humidity and dust. If porosity specifications are to be assured, 100 per cent X-Ray is dictated. Fortunately, these alloys can be welded repeatedly without any deleterious effects.
- (3) Until recently, 9 per cent nickel was not acceptable for service unless the welds were stress-relieved, which eliminated its use on large structures for all practical purposes. However, recent changes in the codes (ASME Code Case 1308) permit 9 per cent nickel, which is quenched at 1475°F and tempered at 1050° to 1125°, to be used in welded cryogenic pressure vessels without stress relieving the completely fabricated vessel.

Taking all factors into consideration, the use of aluminum alloys (5000 series) is preferred for prismatical, ship's tanks. Specifically, alloys 5083 or 5456 containing from 4.5 to 5.5 per cent magnesium and up to 0.8 per cent manganese are superior for this application.

#### Safeguards in Materials Manufacture

Once the material is selected the design engineer must be on guard for inexcusable, sloppy mill practice:

- (1) The design engineer should specify precisely what test specimens must be taken and how many. A chemical analysis of each run is also required.

- (2) In annealed material, it is not uncommon practice to "stretch" the plates that come-out of the annealing furnace bowed (because of inadequate support). This practice should not be acceptable under any circumstance where annealed temper is specified.
- (3) Rolled-in metal resulting from failure to keep the rolls clean cannot be tolerated in an optimized structure.
- (4) Ultrasonic inspection around the edges of the plate should be performed.
- (5) More uniform properties can be achieved in extrusions if a larger capacity press is used so that the extrusion can be carried out at a lower temperature.
- (6) Suppliers that are willing to guarantee properties above the minimum standards for the industry invariably expect compromise on the preceding items.

The mere statement from a supplier that the material will be manufactured according to "tight" aircraft standards is in the author's experience not sufficient to guarantee the quality that can be obtained by exercising a little more care. Apparently aircraft standards are not as tight as they sound.

#### Final Inspection

Finally, the design engineer should participate in all aspects of the fabrication, including the qualification of the welders and ultimately the hydrostatic pressure tests. Even though the welds are 100-per cent X-rayed, the final structure should be dye-checked. Because neither the X-ray nor the dye-check will indicate the presence of small crater cracks, a visual inspection with a magnifying glass should be made of all welds and repairs made where indicated before the tank is put into service.

#### Design for the Insulation System

The design of the insulation system will be described only briefly, particularly with respect to its effect on the design of the tanks. Figure 10 shows the general arrangement for the tank and insulation. It will be noted that the insulation is attached to the inner hull of the ship. The following requirements have to be met:

- (1) The owner specified that the insulation system must be liquid-tight in the remote event that the inner-liquid containing tanks should spring a leak. The owner has a considerable investment in the ship, and he is not willing to endanger the ship's structure by its coming in contact with the cold liquid. In other words the insulation should serve as a secondary barrier, and therefore must be inert to the liquid.

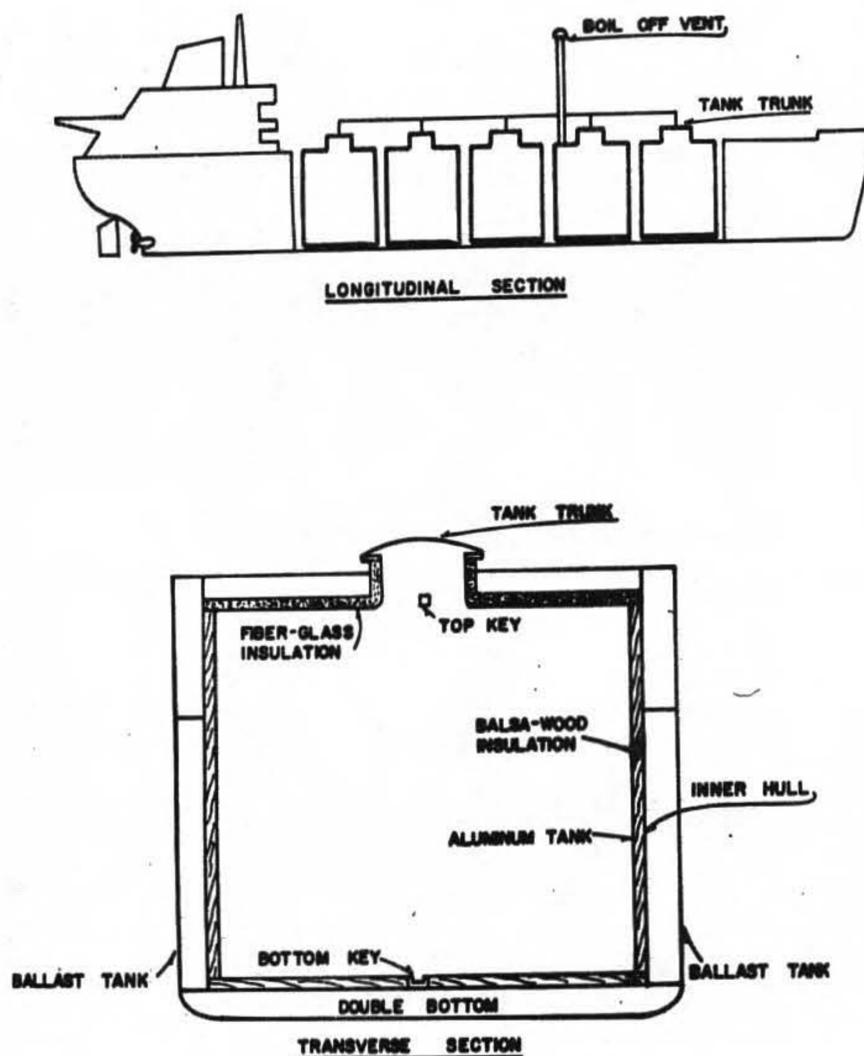


FIGURE 10: CROSS-SECTIONS OF A VESSEL SHOWING PRISMATICAL TANKS.

(2) The bottom insulation should be of sufficient strength to transmit the enormous stresses (due to the ship's motion) at the bottom key of the tank into the ship's structure.

(3) In the event of a fire on board ship, it is desirable that the insulation be able to maintain structural integrity when its outer face is exposed to a temperature of  $1200^{\circ}\text{F}$  for at least four hours. Considering that the inner face will be at  $-250^{\circ}\text{F}$ , the requirements are very severe.

So long as all of the above requirements have to be met, most insulating materials within economic reach are immediately eliminated. Foamglas offers a possibility except that it tends to become friable at low temperatures (not desirable in the case of racking in the ship). Furthermore, since the ratio of its yield stress to thermal stress is only 0.45, provision will have to be made for expansion joints between the panels of foamglas such that it is free to move in all directions. These expansion joints, like all other joints, are potential sources of leaks. Various foamed-in-place or sprayed-on resins fail to meet the three requirements specified above in addition to not having yield stress to thermal stress ratios of greater than one.

As was stated before, wood is the "strongest" material of construction for cryogenic service. Furthermore, balsa wood is an excellent insulator, and when faced with a thin skin of maple plywood, it is impervious to liquefied natural gas. The biggest disadvantage to the use of wood is that it possesses strong directional properties. For materials like metals, having uniform properties in all directions, stress analyses are relatively simple. On the other hand, in wood one must deal with 3 yield stresses, 3 moduli of elasticity, and 9 Poisson's ratios. Nevertheless the situation is far from hopeless, because here again it is possible to design around the difficulty. If the insulation panels are built-up cross laminations (bonded together with adhesive) wherein the grain orientation of the wood is varied, it is possible to achieve "balanced" construction such that the properties of the finished panel are essentially uniform in two directions. In the case of balsa, there is no alternative since it comes in carefully hand-selected pieces of specified density which average 2 to 4-feet in length,  $3/16$  to  $1\frac{1}{4}$ -inches in thickness, and 2 to 4-inches in width. From these "toothpicks" panels up to 16-feet long, 4-feet wide, and 8 to 12-inches thick are shop-fabricated. These panels are then mounted on the inner hull of the ship, and the individual panels are joined together by plywood scabs.

The thickness of the insulation required is determined by economic factors:

- (1) With increasing thickness the insulation costs increase while the rate of boil-off in transit decreases. A certain amount of boil-off is required if the gas is used to generate steam in the boilers which in turn propels the ship. Therefore, a "controlled-rate" of boiled-off is indicated, and it must be balanced against the cost of other fuels. If the boil-off is not to be burned, it must be reliquefied. A three-way economic optimization of insulation costs, fuel costs, and reliquefier costs are required. Unfortunately the problem is not so simple.
- (2) The optimum thickness as determined in item (1) must be further analyzed. As the insulation thickness increases, the cargo capacity of the ship decreases with negligible savings in smaller tank costs. At first it would appear that this decrease in cargo capacity is trivial. However, one-inch of insulation decreases the cargo capacity

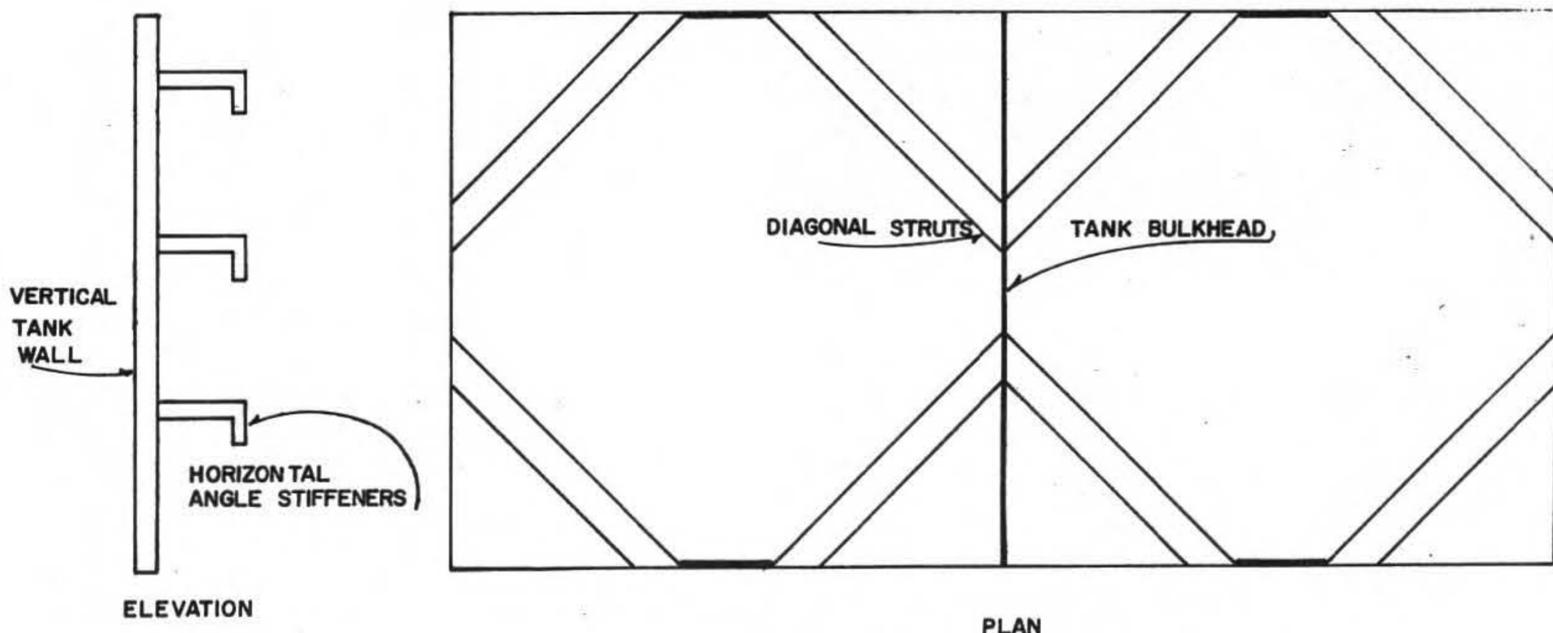


FIGURE 7: HORIZONTAL ANGLE STIFFENERS AND DIAGONAL STRUTS IN SHIPS TANKS.

by more than 1000 barrels, and in terms of profit margins measured in barrels of liquid carried, this figure could be very significant.

- (3) To add further complexities, the thickness of the insulation will affect the amount of heat leak and therefore the thermal stresses in the tanks. Figure 11 shows qualitatively this relation. It is apparent that the minimum thickness of the insulation will be determined by the maximum allowable design stress. Beyond this point the other factors mentioned above come into play.

In summary the thickness of insulation will be influenced by insulation costs, fuel and/or reliquefier costs, cargo capacity, and thermal stresses.

#### Cargo-Handling Equipment

It will have to suffice to say that the cargo-handling equipment, piping, valves, fittings, pumps, gaskets, bearings, instruments, etc. present some very exciting problems. For example, even though aluminum piping would be cheaper, one is almost forced into using stainless steel simply because valves, expansion joints, etc. are only available in the sizes required in stainless steel. Of course, one could consider using aluminum piping and stainless steel fittings, but the junction between these two dissimilar metals which are constantly bathed by a sea spray constitute an almost perfect galvanic cell and the result needs no further elaboration. Of course there are ways to design around this situation but again the factor of economics enters the picture. Aside from this problem, picture a massive super-structure on deck constantly pounded by the sea. Even the piping supports can tax the designer's imagination. The problems associated with cargo-handling should not be depreciated since the total costs here exceed those of either the tanks or the insulation system.

#### Summary

No pretense is made that the foregoing does anything more than to scratch the surface of some of the major problems that confront the design engineer in specifying materials of construction for transportation of liquefied natural gas in ocean-going tankers. Solutions to these problems, other than those presented above, are being studied and development is in some cases at very advanced stages.

The most significant point to be made is that the present status of development would not have been possible without extensive laboratory data and pilot-scale tests. The cost of the development program alone is estimated in excess of 15-million dollars. Despite recent, promising advances in the theory of the solid state, none of this information was of any value, even the plausible theories of rates of crack propagation. In the present state of learning, and in the foreseeable future, there does not seem to be any hope for avoiding the use of what to some may seem as pretty "dirty" numbers to grind out some clean answers which are reliable within a matter of the required few per cent. Remember: the economics are pretty tight!

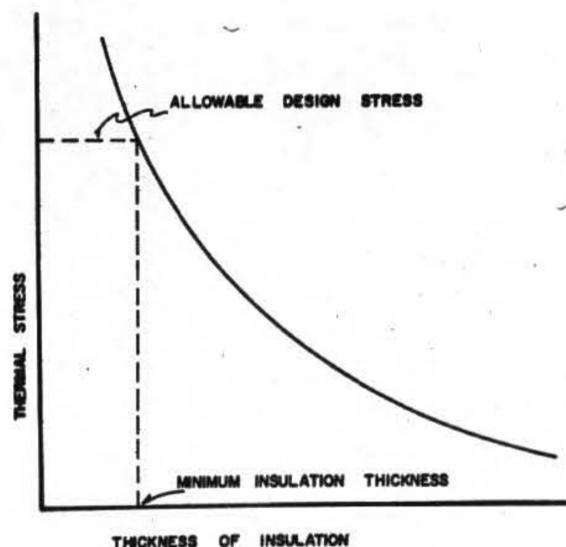


FIGURE 11: EFFECT OF THICKNESS OF INSULATION ON THERMAL STRESSES IN TANKS

## DESIGN AND SELECTION

C.A. Siebert  
University of Michigan

In order to effect a reduction of corrosion through materials design and selection one must understand the underlying principles of corrosion, and the many ramifications which may influence the rate of corrosion of a piece of equipment, or component parts of the equipment.

It is an accepted fact that all corrosion in aqueous media is an electrochemical process, that is, metal passes into solution as metal ions giving up electrons which can be consumed by some other reaction. A metal immersed in an aqueous medium will exhibit a potential which can be measured against a hydrogen electrode or any other half cell such as a calomel or a copper sulfate cell. This potential is referred to as the open circuit solution potential of the metal in that particular environment, and is only a thermodynamic function indicating the tendency for corrosion to occur but is no indication of the rate of corrosion in that environment. The standard E.M.F. series as published in various handbooks and electrochemical textbooks is of little value to the evaluation of a corrosion problem. The potentials listed are for a specific concentration of metal ions of the metal in question, namely one molal concentration. One can compute the solution potential at some other concentration by the equation:

$$(1) E_M = E_M^o + \frac{RT}{nF} \ln a (M^{n+})$$

where

$E_M^o$  = the potential at unit activity of the ions

R = the gas constant

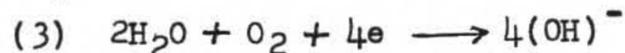
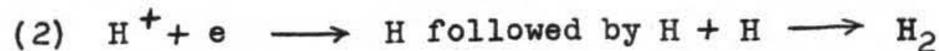
T = the absolute temperature

F = Faraday's constant

n = number of electrons involved in the electrode reaction.

At this time I should like to call your attention to a difference in sign convention which exists between European scientists and many American scientists. The European scientist places gold at the top of the E.M.F. series with a potential of +1.50 volts. The corrosion engineer places it at the bottom as -1.50 volts. This can lead to confusion if one is not careful to determine the sign convention that an author is using in presenting his work. Fortunately, both agree to call the metal of a galvanic couple which is corroding the anode.

If a strip of iron and a strip of copper are placed in a neutral salt solution they will each exhibit an individual open circuit solution potential. If the two metals are placed in electrical contact with each other, a current will flow in the circuit, or more specifically, electrons will flow from the iron to the copper. (Iron is the anode). A measurement of the individual solution potentials of the iron and copper under these conditions would show that the potential of the iron moved toward the copper and that of the copper toward the iron. This is due to polarization and is a function of the current density on the anode and cathode. At the same time depolarization is taking place, that is a reaction to consume electrons at the cathodic areas. These reactions are believed to be



Reaction (2) is the main depolarizing action in acid solution where the pH is less than 4.5, and reaction (3) is the major depolarizing action in near neutral salt solutions. Obviously hydrogen overvoltage plays an important part when reaction (2) is involved.

The anodic reaction cannot proceed at a faster rate than the cathodic reaction; therefore in a near neutral solution which depends on dissolved oxygen for the depolarizing action, the rate of corrosion is decreased mater-

ially by removing the oxygen from the solution. However, anaerobic bacteria can depolarize by removing adsorbed atomic hydrogen from the surface of the metal. In water systems of limited oxygen content this can be controlled by the addition of a few parts per million of chlorine. It is more difficult to control in underground structures, cathodic protection offering some possibility.

Since current density is the controlling factor on the rate of galvanic corrosion, it is highly important that in the use of dissimilar metals in electrical contact with each other the ratio of anodic to cathodic areas be as large as possible.

We have discussed the case of two dissimilar metals in electrical contact with each other. The same condition exists on a single pure metal in that many local anodes and cathodes occur on the surface. These may be due to grain boundaries, impurities, dislocations in the lattice, etc. If one measures the solution potential of the metal with the half cell probe somewhat removed from the surface of the metal, one gets a somewhat integrated average reading for the surface. However, if a fine probe is used close to the surface, then differences of potential will be observed over the surface.

### Galvanic Action

Galvanic action can occur for a number of reasons, some of these being:

(a) Dissimilar metals in electrical contact with each other. This has been discussed above. However, it must be remembered that this same condition can exist in multiphase alloys. Pure metals and single phase solid solution alloys are best for resisting corrosion and multiphase alloys are good if the polarized potentials of the various phases are nearly the same.

(b) Oxygen concentration cells can produce galvanic action. Since dissolved oxygen is necessary to promote the main depolarizing action at the cathodic sites, a lowering of the oxygen content at a localized spot will cause this area to become anodic to the areas which have a readily available oxygen supply. This often causes severe pit type corrosion. Lap joints not properly sealed can suffer accelerated corrosion in the crevices due to the oxygen concentration cell.

(c) Ion concentration cells will exhibit galvanic effects as predicted by equation (1). The area where a higher ion concentration exists will be cathodic to the areas where the ion concentration is low. This can help to minimize the effect of the oxygen concentration cell in pit type corrosion, but it does not counteract it.

(d) Localized cold working of a metal will generate anodic and cathodic areas with the cold worked area being the anode. This can be readily demonstrated by placing a cold headed nail in a solution composed of 20 g. NaCl, 2 g. ferricyanide, and 2 cc of phenolphthalein per liter of water. The head and tip will turn blue and the body of the nail will turn pink. Cold riveted joints and cold bent corners are illustrations of this condition.

(e) The velocity of the corroding medium has an influence on the depolarization of the electrodes. Changes in pipe sizes in a system with the resultant changes in velocity can set up a galvanic action. This may be even more noticeable if the flow changes from stream line to turbulent flow.

The above points out some of the factors which can produce galvanic action and therefore should be kept in mind when designing a piece of equipment.

### Inhibitors

The question of whether or not the process can tolerate the use of inhibitors should always be considered when selecting a material as the use of inhibitors can often effectively reduce the rate of corrosion. Inhibitors are classified as anodic or cathodic depending upon which electrode is affected by the inhibitor. The polarized potentials of the electrodes are altered by the presence of the inhibitor. Inhibitors are further divided into inorganic and organic substances; some require the presence of dissolved oxygen to be effective and others do not. The majority of the inhibitors used today are of the anodic type. The films formed on the surface of the metal are thin and usually invisible and are believed to be either an oxide, or an adsorbed film in the case of some of the organic compounds. Therefore the selection of an inhibitor must take into account whether or not dissolved oxygen is present. It is imperative that a sufficient amount of anodic inhibitor be maintained at all times to get the optimum result, as a breakdown of inhibition at localized spots results in creating small anodes surrounded by large cathodic areas which may be more detrimental than if no inhibitor had been used.

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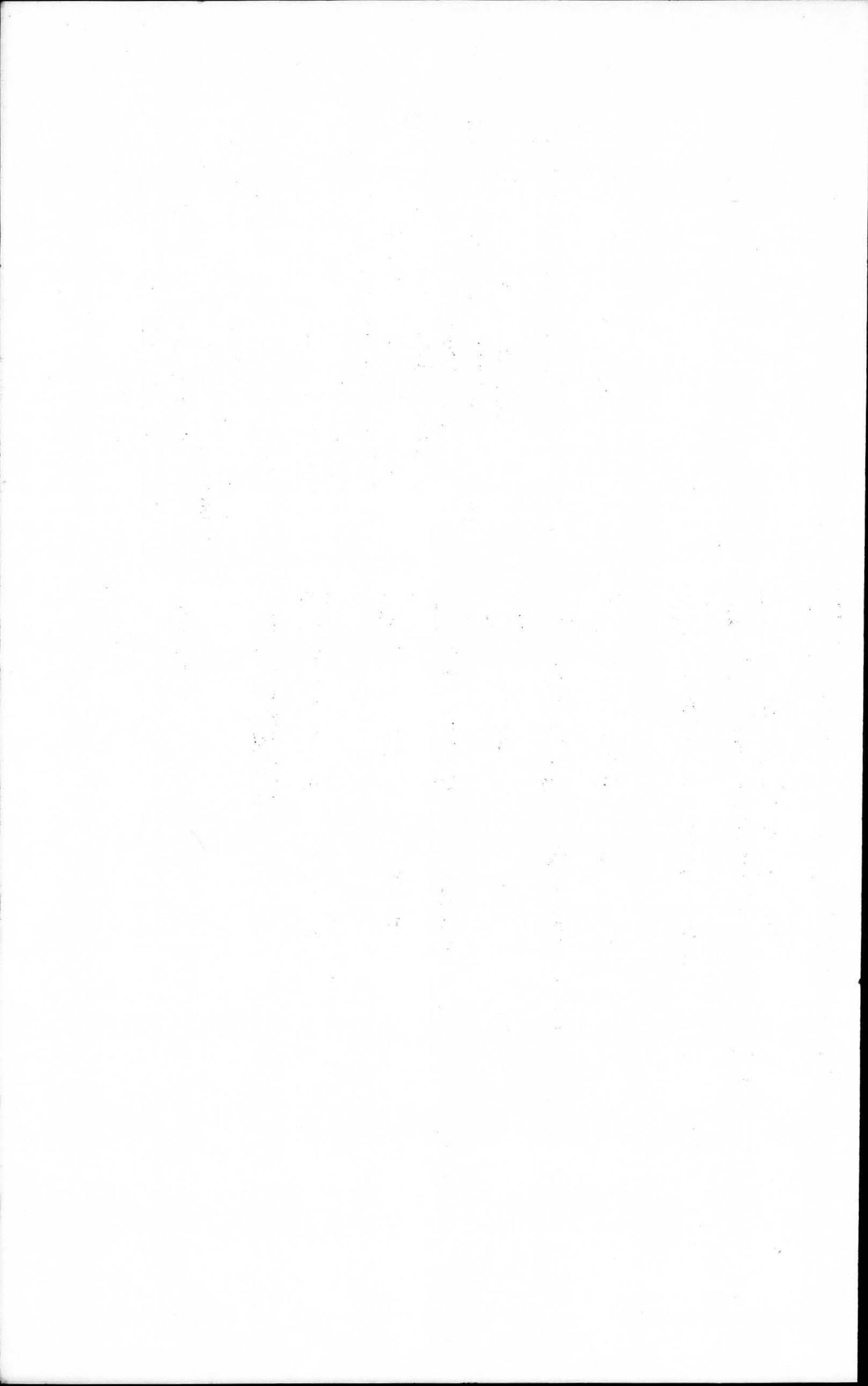
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Some metals develop passivity when exposed to air which is maintained in many solutions providing dissolved oxygen or other oxidizing media are present. In some respects the oxygen appears to act as an inhibitor. Chromium, nickel, and molybdenum are among the metals which exhibit this phenomenon. The stainless steels containing 11.5% or more of chromium have been studied very extensively and many words have been written regarding the nature of the film which causes passivation. The thin films produced by exposure to the air have not been isolated and electron diffraction methods have not shown any definite pattern as to the structure of the film. However, films produced by electrochemical treatment which are thicker indicate a chromic oxide structure. Tests on an annealed 18 Cr 8 Ni type 304 stainless steel in 50%  $H_2SO_4$  solutions at 30°C showed a loss of 0.01 mils per month in an aerated solution and 62.5 mils per month in an air free solution. This and other experiments would lead one to believe that the passivating film must be due to an adsorption phenomenon rather than a chromic oxide film. This is very different from the case of exposing aluminum to air; here a definite aluminum oxide film does form. The passivating film on stainless steels is subject to breaking down in isolated spots in the presence of some ions such as  $Cl^-$  and  $SO_3^{2-}$  ions. The passive areas are cathodic to the non-passivated areas, and the small anodic areas result in severe pit type corrosion. Under these circumstances a molybdenum bearing stainless steel is desirable such as an 18 Cr, 12Ni, and 2-3 Mo, as the Mo additions greatly improve the resistance of the passive film to such localized breakdown.

#### Stress Corrosion Cracking

Stress corrosion cracking must always be considered when selecting a material for a given application. Stress corrosion cracking in general is accompanied by very little overall corrosion and is difficult to detect by visual inspection of equipment. It occurs when high tension stresses exist in some types of corroding media. Stress corrosion cracking has been recognized in brasses and low carbon steels and called season cracking and caustic embrittlement respectively for the two alloy types. The cracking of 70 Cu, 30 Zn cartridge cases while in storage was eliminated when it was determined that residual stresses introduced in the last cold forming operation was responsible for the cracking. A stress relief heat treatment as a final operation reduced the residual stresses to such an extent that cracking was eliminated. The above indicates that externally applied design stresses are not necessary to produce cracking. Residual stress levels in excess of the yield strength of a material are frequently encountered in welded joints. However, the externally applied tension stresses added to localized residual tension stresses may often be the cause of failure. Stress corrosion cracking does not occur when the stresses are in compression.

A large number of investigations have been carried out in the past 15 to 20 years on stress corrosion cracking in other alloys than brasses and low carbon steel. It occurs in alloys where the base metal is Mg, Al, Cu, Ni, Ag-Au alloys, etc. Austenitic stainless steels have received a great deal of attention and some rather interesting facts have been uncovered. For instance they will undergo stress corrosion cracking in the presence of the chloride ion if the solution contains dissolved oxygen but do not when the oxygen is removed. However, they will crack in NaOH solutions regardless of whether or not dissolved oxygen is present.

A few thoughts to keep in mind when selecting a material for a highly stressed application are:

(a) Residual stresses may produce a highly stressed condition where the design stress may be relatively low. Adequate stress relief should be carried out whenever possible to minimize this condition.

(b) Increasing the temperature of the corroding medium will usually increase the susceptibility to cracking.

(c) Shot peening has been suggested as a means of putting the residual surface stresses in compression and therefore preventing the initiation of cracking. This means should be approached with caution as the compressive stresses introduced by the process do not extend to any great depth below the surface, and if general overall corrosion occurs to a limited extent the compressive layer may corrode away. Under these circumstances the start of cracking would only be delayed.

(d) As far as is possible do not use an alloy which is known to be highly susceptible to cracking in the corroding medium which is to be contained by the alloy.

(e) Proper control of solution to insure oxygen or inhibitor control where these have proven effective in preventing cracking.

(f) Stress corrosion cracking has been shown to be due to a localized galvanic action. Therefore the possibility exists of preventing it by the proper application of a reverse current through the use of sacrificial anodes or from a source of D.C. current.

### Intergranular Corrosion

Intergranular corrosion occurs when the grain boundary or area in the immediate vicinity of the boundary is anodic to the body of the grain. This may result from a difference in the polarized solution potential of the grains and boundaries due to precipitated compounds, or to a localized stress existing at the boundary. The grain boundaries of high purity aluminum (99.986% Al) water quenched from 620°C are anodic to the grain bodies in hydrochloric acid, but cathodic when furnace cooled. It is difficult to picture this as due to a precipitated compound at the boundary. On the other hand, there is no doubt the austenitic stainless steels are made susceptible to intergranular corrosion by the precipitation of chromium carbide or sigma phase (iron-chromium compound) at the boundaries. Whether the susceptibility is due to chromium depletion or stresses accompanying the precipitation at the boundary is still open to debate. The essential point is that the material is rendered susceptible to intergranular corrosion by this precipitation process. A 304 stainless steel may be checked by the ASTM standard boiling nitric acid test in the as received condition to determine whether or not it meets the necessary standard prescribed by this test. The steel is normally supplied in the annealed condition, that is, water quenched from 1850-1950°F. However, this steel becomes susceptible to intergranular corrosion when heated in the temperature range of 750-1650°F due to carbide precipitation at the boundary. Therefore welding will produce susceptibility in the heat affected zones of the weld, and stress relieving in the temperature range required by the ASME code (1100-1200°F) makes the entire structure susceptible to intergranular corrosion. In this condition the same material will not pass the boiling nitric acid tests. Susceptibility can be minimized by using Cb, Ti, or Ta stabilized steels, or extra low carbon (.03 C max.), but the use of these steels is no assurance that intergranular corrosion will not be encountered under all conditions. It is somewhat ironical that stress relieving to eliminate stress corrosion cracking in these steels makes them highly susceptible to intergranular corrosion. Any alloy having a precipitated compound at the grain boundary offers potential danger of susceptibility to intergranular corrosion.

### Cathodic Protection

Cathodic protection is used quite extensively to reduce corrosion of engineering structures. This is accomplished by the use of sacrificial anodes such as Mg-Zn alloys, or a reverse current from a source of direct current. Protection of this type is used on underground pipe lines and other underground structures, water tanks, sea-going vessels, offshore petroleum operations, etc. The type and amount of protection needed is a function of the corroding environment and metal to be protected and is only determined by a careful survey of the conditions prevailing. The possibility of using this means of reducing corrosion should be considered in the selection and design of equipment.

### Cavitation

Severe damage may occur to the surface of a metal when subjected to fluids at varying velocities and pressures. Euler, in 1754, predicted the loss in efficiency of turbines when operating at high speed due to the formation of bubbles in the low pressure areas. At that time he did not foresee the resulting damage that can occur when the fluid enters a high pressure area and the bubbles collapse. The calculated pressures released by the collapsing bubbles are from several hundred to several thousand atmospheres depending upon the assumptions made for the calculations. Needless to say, the forces are great enough to produce severe pitting and loss of metal in the areas where the bubbles are collapsing. Slip lines, indicative of plastic deformation, have been observed in the microstructure of the metal at the base of these pits, and cracks, which may be due to fatigue, have also been observed in severely damaged metals. Pumps, valves, turbines, propellers, etc. are all subject to this kind of failure when the proper flow conditions are encountered to produce cavitation in the fluid. It is impossible to describe cavitation resistance in terms of some mechanical property of the metal at the present time. For case histories on the subject the reader is referred to "Cavitation Damage," A.S.M.E. 1956. In this paper an effort was made to point out some of the factors which have an influence on corrosion rates.

In conclusion may I point out that the reduction of corrosion through materials design and selection depends on many factors, and the selection of a material for a given application based upon corrosion data reported in some compilation of corrosion data can lead to sad results if the test conditions did not duplicate the conditions encountered in service.

## MATERIALS INSTRUCTION FOR CHEMICAL ENGINEERS

### What Should Be Taught By The Physical Chemist?

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In the design and development of new processes, the chemical engineer must make a choice from various possible construction materials. Twenty or thirty years ago the problem of suitable construction materials was relatively simple compared to some present day problems. The growth of our technology is continually requiring new and better construction materials, particularly in the areas of nuclear energy development, the direct conversion of heat into electrical energy, and space flight development. Where once a relatively few metals such as iron, nickel, aluminum, copper, lead, zinc and some of the noble metals were of primary commercial importance, today practically all the elements have taken on a new importance in various phases of commercial development. The chemical engineer may be concerned with processes operating at liquid helium temperatures, a reactor core which hopefully can operate at 1500° to 2800°C, the reprocessing of reactor fuels using a fused salt and liquid metal as solvents instead of the more usual aqueous and organic solvents, or processes involving ultra high vacuum or extreme pressures. Many potentially useful concepts cannot be developed because suitable container or construction materials are not available. Conversely, the availability of better construction materials can open up new fields and permit development of new and more economical processes.

The service behavior of a material involves an environment, and its serviceability will be determined by its interaction with the environment as well as its mechanical properties, both of which will depend on chemical kinetic and physical factors. From a chemical point of view, containers or construction materials are additional components in a heterogeneous system which must not take part in a deleterious way with the reactions or processes of interest. From a mechanical point of view, the construction materials are members or units of a structure or device designed to withstand various mechanical stresses and perform some useful purpose. The chemist or physical chemist is more interested in the chemistry, chemical kinetics, surface phenomena, and phase equilibria involved. The mechanical engineer is more interested in the static and dynamic characteristics of the unit, how the various pieces fit together and the elastic, creep, fatigue, wear-resistance and other properties of the construction materials. The chemical engineer should have some appreciation of both of these areas. It is in the first area that the physical chemist can contribute most to the chemical engineer's training. The wide range of available metals, alloys, refractories, cermets, composite materials, etc., and possible environments precludes emphasis of any one type of material or environment. The training program which will be most effective in preparing the chemical engineer to cope with the materials problem is, of course one which emphasizes basic scientific and engineering principles. The basic principles or theories involved cut across many branches of science or engineering. With the growing complexity of our technology, new branches are added and there is always a great deal of controversy as to what the scope of the new branch should be and whether it will grow or eventually wither away. Chemical engineering has been established for a sufficiently long period of time that it is perhaps safe to say that the primary concerns of the chemical engineer are the unit operations, chemical reactions and kinetics and the physical processes such as heat and mass transfer for the particular process to be developed. The selection of suitable construction materials, although very important, is only one of his problems. The development of new and better alloys, ceramics, refractories, semiconductors, etc., is more appropriately a problem for the metallurgist, ceramist, or the material scientist, and the development of better plastics, fluorocarbon resins such as teflon and related materials is more appropriately a problem for the organic chemist. Nevertheless the chemical engineer should have some knowledge of the utilization and limitations of construction materials and some understanding of their service behavior.

Chemical engineering curricula require basic courses in chemistry, physical chemistry, physics, and mathematics which form a basis for understanding the behavior of matter and a background upon which a more detailed knowledge of materials can be developed. Even without exposure to materials problems in chemical engineering courses or a special course in materials the student has the background to enable him to make various broad generalizations in this area. He is well aware from his training in chemistry as well as experience that some materials react vigorously with water or air while others are relatively inert. From his study of free energy and the equilibrium constant, he is aware that the reaction of water or atmospheric oxygen with most metals, alloys, and many other materials is thermodynamically favorable. His introduction to chemical kinetics and the effect of temperature on reaction rates serves as a basis for understanding why many of these materials are stable in air at ordinary temperatures. Similarly, he can conclude that iron is able to form a suitable container for a dry alkali metal chloride since the displacement of the alkali metal by iron is thermodynamically unfavorable and the iron will remain in the reduced state. His study of heterogeneous equilibria and phase diagrams enables him to conclude that although metals A and B

have the requisite strength for service at a given temperature, a structure with A and B in contact will fail if these metals form a eutectic which melts below the proposed operating temperature. Molten salts as well as molten alloys have been proposed as nuclear fuels. The selection of a suitable metallic container requires knowledge of the thermal conductivity, nuclear properties, mechanical properties, the alloying behavior and reactivity of possible metallic container materials. The same problems would have to be considered in the case of a nonmetallic container.

There is probably little or no disagreement that the material covered in the usual one-year course in basic physical chemistry is pertinent to the materials problem as well as other phases of chemical engineering. Examination of undergraduate physical chemistry texts will show that the material covered is rather extensive. In many cases, such as the text, "Physical Chemistry", by W.J. Moore, Prentice Hall, the material included in the text is admittedly more than can be profitably discussed in the usual one-year course. Incorporation of additional material would mean a less advanced or less thorough discussion of other important topics. Further training in thermodynamics, theory of rate processes, alloy theory, corrosion, etc., would certainly be desirable. If two semester courses could be devoted to this area in the undergraduate curricula, a number of possibilities exist. An additional semester devoted to basic physical chemistry, or a semester course in chemical thermodynamics, thermodynamics of solids or physics of solids followed by a one-semester course in physical metallurgy would be very helpful in strengthening the student's background.

Since metals and alloys are the most commonly used construction materials in chemical processing, an introductory course in physical metallurgy would be very worthwhile. There are various texts available that could serve as a basis for such a course. An outline of material to be covered might be as follows:

1. Electronic structure of the elements.
2. Types of bonding, ionic, covalent, metallic; introduction to the free electron theory and band theory of solids; classification of solids as conductors, semiconductors and insulators.
3. Crystalline nature of solids, crystal geometry and classification of crystals; x-ray diffraction techniques.
4. Correlation of physical properties with crystal structure and type of bonding.
5. Imperfections in crystals.
6. Diffusion in solids.
7. Interpretation of phase diagrams and their correlation with the microstructure of alloys; effects of heat treatment with special emphasis on iron-carbon alloys.
8. Work hardening and recrystallization, nucleation and growth, age hardening, martensitic transformations, brittle-ductile transitions, radiation hardening, dispersion hardening.
9. Introduction to theories of creep, fatigue and fracture.
10. Cermets and high temperature refractories.
11. Corrosion and corrosion mechanisms.

The degree of emphasis to be given to the various topics and the extent to which nonmetallic materials should enter into the general discussion will depend on the background of the student and the time allotted for the course. Various texts can serve as a guide to the extent of coverage and level of treatment that may be considered suitable for an advanced undergraduate course. Some texts that may be considered for this purpose are: "Elements of Physical Metallurgy", by A.G. Guy; "Physical Chemistry of Metals", by C.S. Darken and R.W. Gurry; "Physical Metallurgy", by Bruce Chalmers; "Physical Metallurgy", by C. Ernest Birchenall; "Theoretical Structural Metallurgy", by A.H. Cottrell; "Solid State Physics", by A.J. Decker; "The Solid State for Engineers", by Maurice J. Sinnott; "Elements of Material Science", by Lawrence H. Van Vlack; "Thermodynamics of Solids", by Richard A. Swalin; and "Mechanical Metallurgy", by George E. Dieter, Jr. A recent review of theories for creep, fatigue, fracture and the mechanical behavior of materials is given in "Mechanical Behavior of Materials at Elevated Temperatures", edited by John E. Dorn. Another possibility is a two-semester course based on a text such as "The Solid State For Engineers", by Maurice J. Sinnott. This text has been written for the specific purpose of introducing to the engineer the basic principles which underlie the behavior of solids.

Whether such courses are to be taught by a physical chemist, metallurgist, chemical engineer or other qualified persons is not important. The primary emphasis should be on general principles. This is not intended to imply that training in basic principles is all that is necessary for the practical application of engineering materials. As already indicated the problem is complex and it is not yet possible on the basis of first principles to predicate in detail the behavior of a material under various service conditions. Knowledge of what materials or classes of materials are available or have been used successfully for various types of service, methods of testing and evaluating materials for a specific use, and economic factors are equally important. Training in this area is more appropriately covered in engineering courses.

# What Should Be Taught By The Engineer?

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Ideally, the teaching of Materials Science or Engineering Materials by engineers is unnecessary but in the same sense that all of engineering is unnecessary. Engineering has been defined in many ways, but the essential features of any definition generally incorporate some words dealing with the laws of nature, economics, the benefit of mankind and judgment. Materials obey certain physical laws, economics is involved in their use, benefits are derived from their use, and judgments have to be made in their use so, by definition then, Materials does fall within the scope of engineering. Given conditions where the laws of nature are known, economics is fully understood, and the benefits to mankind are clearly evident, there is not much left to the exercising of judgment, and the need for engineers would disappear. This is not likely to happen in the foreseeable future, so we can dismiss the ideal case and get to the case at point.

If engineering consists of a mixture of mathematics, science, economics, utilitarian ends and judgments, can't this be simply broken into its component parts, be taught by specialists, and then be brought together to produce engineers? The answer is that this is essentially what we do in our various engineering curriculums. The mathematics and sciences are taught in the early years, their economic application, the development of judgment in making alternate choices occur later in the programs. In terms of ECPD accreditation, the sciences, engineering sciences, then the analysis, syntheses and design.

Where does Engineering Materials fit in these curriculums? Not in the early years with the sciences since it is not a science, but an engineering science. It is different from the usual engineering sciences in that instead of being based only on physics, is also based on chemistry. It is this dual base that causes so much difficulty in teaching Engineering Materials. Most engineers, with the exception of the Chemical, Metallurgical and Ceramic groups, elect only one year of chemistry while the chemistry that is needed is Physical Chemistry and this, in most schools, is not a first year chemistry course. The Chemical Engineers then as a group have a decided advantage over most other engineers in that they have the science base on which a good materials course can be taught. A further advantage in most chemical engineering curriculums is that they invariably have course work on Thermodynamics and Rate Operations and both of these courses provide an additional set of foundations for the materials course work.

Given then a person with training in mathematics, physics, chemistry, thermodynamics, possibly rate-operations, and engineering science training in mechanics and strength of materials, it isn't a particularly difficult task to put together a Materials Science or Engineering Materials course that has real depth and meaningfulness.

One of the first things to be done before discussing what to teach chemical engineers is to determine the scope of the materials field. To many engineers the word materials means the selection of a substance for a particular application. To an electrical engineer it is the electronic properties of conduction, semi-conduction, insulating or magnetic properties. To a mechanical engineer it is a structural material with the emphasis on the elastic, plastic or shock resistance. To chemical engineers it is a structural material but subjected to corrosive environments. So it goes on down to a civil engineer to whom materials means concrete, asphalt and reinforcing bars. These engineers are primarily concerned with the specification of materials for various end uses.

Another group of engineers, equally as large or even larger, are interested in the manufacture and production of materials. These are primarily chemical, metallurgical and ceramic engineers whose principal concern is to prepare or take given raw materials and to convert these into intermediate products which are to later appear in some finished form. Steel, petroleum, plastics, textiles, paints, cements, solvents, etc., are but a few of what might be termed the materials industries but are more commonly known as the chemical industries.

A third group, usually chemical, metallurgical or mechanical engineers, are concerned with taking materials in bulk form and in fabricating them to finished shapes for direct use by other engineers. Casting, extruding, forming, blending, treating and in general processing them for ultimate use.

These last two groups, in addition to knowing enough about materials to specify them for use, must also know how to manufacture, process and treat these materials so they will have the required properties for ultimate usage. This is a much more severe requirement than simply knowing what the ultimate properties are, and as you will note, chemical engineers are predominantly active in these second and third groups. It is for this reason that I believe that the materials book given to a chemical, metallurgical or materials engineer should be pitched to a higher level than one would give to civil, electrical or mechanical engineer. These other fields would certainly profit from a more intensive treatment of materials science, but their lack of preparation, principally in chemistry and thermodynamics, makes this an extremely difficult teaching assignment.

What should chemical engineers be taught about materials? My viewpoint is that they should be taught from as basic a standpoint as is practicable with a view to understanding why materials have certain properties, rather than attempting to teach them how to produce, process or specify materials. Knowing the why, one can usually deduce the how, while the converse is not true. One occasionally gets into arguments with scientists about this point. Some feel that it is their job to teach the why, and the engineers' job to teach the how. This may have been true in some cases in the past but is not true of many engineering fields today. There are differences, of course, between scientists and engineers but the teaching of why's and how's is not the distinguishing feature. To me, the principal difference between the two is this: a scientist generalizes while an engineer must particularize. Solid state physicists are quite content with order-of-magnitude agreement between theory and fact, and chemists are practically always concerned with thermodynamic equilibrium. As engineers, however, we can't design processes to orders of magnitude and we are more concerned with kinetics or the rate of approach to equilibrium than we are with where it is. True, we need the science to tell where we are going, but how we get there is our problem. There is a vast difference between knowing about materials from a physics and chemistry standpoint and knowing about them from an engineering standpoint. We must be familiar with the sciences but the scientists can and do get along very well without the engineering.

Materials have a chemical constitution and therefore chemistry is certainly important. They do exist in various environments: electrical, magnetic, mechanical and thermal fields, and they will obey certain physical laws, therefore, physics is important. If crystalline, structure is important; if non-crystalline, the degree of lack of structure is important, etc. It is quite fruitless to argue which is the more important since if they yield useful information, the engineer can use them; maybe not in the way the scientists think they should be used, but nevertheless, he uses them. Another way of stating this I heard from the late G.G. Brown: "A scientist is one who solves the problems he can solve while an engineer is one who solves the problems he must solve." This is certainly true in regard to the materials field. The physicists work almost entirely in those fields where properties are determined by electrons such as conduction, semi-conduction and magnetism. Chemists are a little broader and more apt to be experimentalists, but their efforts are more along the lines of analysis, studies of non-stoichiometry, phase equilibria, etc. Important studies it is true, but not important to the engineer until they become useful.

The principal reason then engineers should teach materials science is that they are in a better position to judge what are the useful parts of the various sciences that are applicable to this field. For example, many materials are classified as crystalline solids, therefore a knowledge of crystallography is necessary. The whole load such as one would get in a typical two-course sequence in Mineralogy or Geology? Obviously not. There is nothing wrong with these elections; one can even make a strong case for such a program. It is just that there are large portions of this work that are of no direct usefulness, now or in the near future, for the engineer. The parts we need, we need badly but not to the extent that we would elect the entire package. Since crystallographers are usually adamant about modifying the existing course we extract the applicable parts and teach it ourselves. This same extractive operation is carried out on various portions of chemistry, physics, and even engineering courses, to yield a body of information which can be called materials science.

Chemical engineering students certainly obtain a surfeit of thermodynamics in their training. It occurs in the early heat and material balance courses, in the physical chemistry, in the regular chemical engineering thermodynamics courses. The difficulty in using this in materials science instruction is that for the most part all this prior work is in the liquid or

gaseous state, and the student has to be shown its applicability to the solid state. The extensive training most engineers receive in engineering mechanics has to be reoriented from the macroscopic scale to the microscopic. In many respects a course in materials science consists in nothing more than taking material previously presented in a different context and reorienting it, adding new application information and welding the mixture into an engineering course. To insist, as many scientists do, that this can't be done is to deny reality. It's done because it has to be done. We can't afford the time for the unhurried, comprehensive, historical, and rigorous approach that they insist upon. The fields of metallurgical and ceramic engineering are two which were formed largely because they did not constitute a respectable part of either chemistry or physics since their subject matter didn't obey the rules. Because of industrial and engineering pressures for improved materials of these types, they became engineering disciplines and were forced to develop their own science along with the engineering applications. Their success in accomplishing this is largely responsible for the current enthusiasm of solid state physicists and chemists for working in these fields.

As in all engineering courses, the syllabus of a course on materials science for chemical engineers changes from semester to semester as new developments occur. Of the order of one-half of the material doesn't change and this is the basic science. Topics such as atomic and molecular structure, crystallography, phase equilibria, thermodynamics, kinetics, bonding and electron theory make up the bulk of this material. The teaching of this material does not introduce any new material to the chemical engineer; he has touched on much of this in several courses in physics, chemistry and engineering. The transition from the macroscopic to the microscopic scale in elasticity and plasticity and the introduction to lattice defects opens up the whole concept of defect structures which is so important to the understanding of many solid state phenomena. The extension of electron theory to zone theory and the concept of electronic defects leads to electrical and magnetic phenomena. Having discussed the influence of electrical, thermal, magnetic and stress fields on solids, it's an easy step then to discuss the tensorial relationships between these to pick up the cross-effects such as thermoelectricity, piezoelectricity, magnetostriction, etc. In the development of this work the emphasis is always on the usefulness relative to engineering with engineering applications stressed wherever possible.

More recently emphasis has shifted towards the structure of liquids and its applicability to polymeric materials and amorphous materials such as the glasses. An area which is fast developing is that of surface phenomena. Its relevance to engineering problems in oxidation, corrosion, catalytic activity, lubrication, wear, etc., are treated although this subject matter is nowhere near as well developed a body of information as the bulk properties, yet it is probably of more immediate significance to the engineer than the bulk properties.

You will note from this brief description of the course that is taught to chemical engineers that this is not a course in how to specify materials, how to make them or how to process them. It is aimed instead at trying to understand why they have certain properties and why processing or treating them can modify these properties. Subsequent course work builds on this course and deals more specifically with metals, ceramics, plastics, etc. While I see no reason why this course could not be taught by non-engineers, it is my feeling that in order to bridge the gap between the science and the engineering it would take someone with an engineering background since the principal gain is to engineering, not to science.

