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PRACTICAL REASONS FOR INVESTIGATING ION TRANSPORT IN HIGH TEMPERATURE INSULATING MATERIALS

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PRACTICAL REASONS FOR INVESTIGATING ION TRANSPORT IN
HIGH TEMPERATURE INSULATING MATERIALS*

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ABSTRACT

Practical problems encountered in a number of advanced technology applications, particularly those related to energy conversion, are discussed. Refractory ionic compounds which are abundant and of high melting point are listed, and technological problems are discussed in terms of specific materials problems. The argument is made that basic information concerning transport properties in refractory compounds is lacking to such an extent that it is difficult to design and assess advanced energy generation systems. Technology applications include a) ceramic nuclear fuels for high temperature fission reactors, b) high temperature gas turbine blades, c) insulators in controlled thermonuclear reactors, and d) magnetohydrodynamic generators. Some of the difficulties inherent in making transport property measurements at high temperatures are also listed.

Les problèmes pratiques rencontrés dans de nombreux domaines avancés de la technologie, en particulier ceux liés à la conversion énergétique, sont discutés. Les composés ioniques réfractaires abondants et à température de fusion élevée sont énumérés et les problèmes technologiques

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sont ramenés à des questions spécifiquement liés aux matériaux. On montre que l'information de base concernant les propriétés de transport dans les composés réfractaires manque au point qu'il est difficile de concevoir et d'évaluer les systèmes nouveaux de production d'énergie. Les applications technologiques comprennent a) combustibles nucléaires céramique pour réacteurs de fission à haute température, b) pales de turbine à gaz à haute température, c) isolants pour réacteurs à fusion contrôlée, et d) générateurs magnétohydrodynamiques. Certaines difficultés inhérentes à la mesure des propriétés de transport à haute température sont énumérées.

1. INTRODUCTION

When ionic crystals are mentioned the first class of materials that comes to mind is the alkali halides. The reason for that is that they have been model materials for basic research and for developing sophisticated techniques of studying crystal physics and chemistry.¹ For example, defect production by radiolysis is now rather well understood, primarily due to work with alkali halides. The relation between diffusion and ionic conductivity has been studied extensively in alkali halides and many of the techniques of modulation spectroscopy, multiphoton spectroscopy, optically detected paramagnetic resonance and vibronic spectra were first studied in these materials.

In spite of the very rich harvest of results of basic scientific interest, few practical technological products² have been developed using alkali halides. The public that supports our research through various government agencies--and this is particularly apparent in the U.S.--is beginning to ask questions such as "Why isn't this research done on materials of greater technical interest?".

The answer is simple; it is more difficult to do experiments and to interpret the results for a ceramic compact than for a clean cubic single crystal such as NaCl. Nevertheless these critics may be in part justified and there may be some very interesting exploration to be done with "more practical" materials. Moreover, in recent years crystal growth techniques have been developed to the extent that a number of refractory oxides can be obtained as large single crystals.

I will describe some of the trends of advancing energy technology, with particular emphasis on materials use and materials problems that are in most cases the limiting factors for the technology. It should become obvious from this discussion how important it is to use the insight and techniques developed during the course of alkali halide research for investigations of refractory insulators.

II. THE GENERAL PROBLEM

In Table I are listed a number of methods of converting energy of fuel into electrical energy. In the upper half of the table--above the dashed line--are the methods in use at the present time: steam electric, using coal as fuel; nuclear reactors, using Uranium 235; and turbines, using natural gas or liquid petroleum fuels. The operating temperatures of these methods are all in the range 500-900°C, where standard steel alloy metallurgy has allowed development of materials that are compatible with steam, water, hot gases and even rather heavy neutron irradiation.

The problem we all are facing is best illustrated by Fig. 1 which shows the rapid increase in energy consumption.² Mankind will have to find a way to level off this curve for two reasons: 1) there is a limit to the available energy sources and 2) there seems to be a direct correlation between energy use and pollution and we are already feeling the effects of pollution in many places.

One way of gaining time before the inevitable necessity of changing our energy wasteful life style in a radical way is to use energy resources more efficiently. This requires that more electricity be generated from the same amount of fossil or nuclear fuel, a goal which requires more advanced technology.

The operating temperature of present day power generating plants is $\approx 600^{\circ}\text{C}$ or 900°K . The first and second laws of thermodynamics show that the theoretical maximum electrical power, W , that can be obtained from a heat source is given by the relation

$$W/Q = 1 - \frac{T(\text{sink})}{T}$$

where Q and T are the heat flow and temperature of the heat source and $T(\text{sink})$ is the heat rejection temperature of the generation system. If $T = 900^{\circ}\text{K}$ and $T(\text{sink})$ is 300°K the very best that theoretically can be done is to transform $2/3$ of the heat to electricity and to reject $1/3$ to the environment. In practice one can never reach such efficiencies and the best plants today use a bit less than $1/2$ of the heat content of the fuel. Now consider the lower half of Table I: If we could build a power plant to operate between say 2100°K and 300°K , the Carnot efficiency would be 86%, and we could hope for practical efficiencies of better than $3/4$, so that only $1/4$ of the heat would be rejected to the environment, rather than more than $1/2$, as is the case now.

Different arguments could be given for some of the other technologies shown in the lower half of Table I. Breeder reactors and Thermonuclear power obviously will increase the world's fuel supplies many times over, if societies are willing to live with the hazard of highly radioactive fission products and toxic fissionable transurancies.

At any rate the temperatures and ambient conditions in which materials must perform as desired for the life of a generating plant are respectively higher and more hostile in any of the advanced technologies than in those presently used.

What types of materials would survive? The most obvious characteristic is that they must have high melting points. In Table II are listed a number of high melting materials, and it is clear that by far the greatest majority of these materials are ionic compounds. Moreover, except for carbon, elemental materials with high melting points are comparatively rare in nature, particularly as compared to materials such as MgO , SiC and Al_2O_3 , which are easily produced from abundant materials. Those compounds on which significant work has already been done are indicated by brackets in the table.

We will now consider the advanced energy technologies given in the lower half of Table I.

III. ADVANCED NUCLEAR TECHNOLOGY

Consider reactors operating at elevated temperatures. The fission products that are produced in the fuel are mobile. To contain the fission products materials which minimize fission product release must be found for containment shells. Also due to fission product mobility in the fuel these product elements will aggregate, causing swelling and other dimension changes. Very little basic research has been done to help us predict what materials and what conditions might minimize fission product release from fuels and dimensional change in the fuel. The type of experimentation that would be extremely helpful is shown in Table III.

To illustrate another problem we will consider a specific example of the effect of temperature gradient. One fuel concept that is being developed for high temperature gas cooled reactors³ is illustrated in Fig. 2. The fissionable material, for example UO_2 , is in the center of the pellet, surrounded by porous carbon (to act as a sponge for fission produced gases) which in turn is surrounded by dense pyrolytic graphite. Unfortunately pyrolytic graphite is not an adequate

diffusion barrier for all fission products, but shown on the right is a pellet that has in addition a layer of SiC as a further diffusion barrier. The layer of pyrolytic graphite in the surface is to strengthen the SiC which does not bond well enough to the inner pyrolytic graphite to withstand the high pressures of accumulating fission gases. Keep in mind that these pellets are extremely small--only about 1/2 mm in total diameter. Nevertheless, the oxides used have a limited thermal conductivity and hence large temperature gradients occur since the heat is created at the center of the pellets and removed at the surface. Fig. 3 shows what can happen to the central UO_2, ThO_2 component of such a pellet. The pellets shown are simply covered with porous and dense graphite, but the same thing occurs in pellets that have a SiC layer in addition. After the pellet has been in a reactor loop at approximately $1350^\circ C$, the central component of the left pellet (UO_2) is no longer at the center. Interestingly enough, in a pure ThO_2 sample this movement of the central component is much less, perhaps because the temperature gradient is less due to the absence of fission in ThO_2 . This effect is not well understood. Apparently if UC rather than UO_2 is used as the fertile central core of a pellet the effect is less drastic. An understanding of these effects require basic studies of the mobility of actinide compounds in irradiation fields and temperature gradients, as indicated in Table III, No. 5 and 6.

IV. ADVANCED GAS TURBINES

Present day turbines can operate up to about $900^\circ C$, if gas flow is adjusted to cool the metal plates and keep the hottest gases away. This is difficult and produces inefficiencies. With ceramic blades and structural materials, flames can go up to above $1500^\circ C$, and the air flow design can be simplified. Just within the last year or two engineering experiments⁴ have begun to indicate that Si_3N_4 and perhaps also SiC might have properties that

would allow them to be used as flame guides and turbine blades. However, ceramics are brittle and in a turbine may be subjected to very sudden changes in temperature-- for example, when fuel for the flame is shut off but the cold oxidizing gases continue to blow on the hot surfaces. Thus changes in mechanical properties due to impurity diffusion, recrystallization or other thermally activated reaction could be catastrophic. Moreover, the blades operate near 1500°C in a gas mixture that is usually oxidizing but which also contains carbon and sulfur gases. According to present knowledge Si_3N_4 is protected by a layer of SiO_2 , so that the corrosion and degradation of the turbine blades may be highly dependent on rate of carbon and sulfur diffusion across a SiO_2 layer. Also for these turbines, as for the case of the reactor fuels described above, large thermal gradients occur which may be instrumental in enhancing ion motion and causing recrystallization and surface reactions to take place. Thus, for this area basic research of the type outlined in Table IV would be very useful.

V. THERMONUCLEAR FUSION

Power from thermonuclear fusion is still in the stage at which the feasibility of obtaining a hot plasma has yet to be demonstrated. However, it is clear that if machines are to be built, enormous materials problems must be solved. A number of institutions are beginning to work on metals related problems such as sputtering off the containment walls, tritium transport through pipes, compatibility of Li fuel and coolant and the containment wall. However, insulators also have to be used. Table V is a list of some applications of insulators for two fusion reactor concepts.

The insulator compounds would be at the temperature of the first wall, which may be around 1000°C. In addition there will be extremely intense charged particle bombardment with resultant current flows. Therefore, the

same types of basic experiments given Table III and IV on a variety of high temperature materials are needed. Note, for example, that materials such as MgO, SiC and the others mentioned before, are all of relatively low atomic number, compared to the iron group and even V or Ti which may be the eventual wall structural material. The low Z may be necessary to minimize plasma quenching due to contamination from sputtered wall material.

VI. MAGNETO-HYDRODYNAMIC GENERATORS

For magneto hydrodynamic extraction of electricity from coal the most promising concept pursued by a number of countries⁵--The USSR actually has an experimental plant running--is diagrammed in Fig. 4. In the combustor fuel which, it is hoped will eventually be powdered coal, is burned with preheated air. The fuel is also seeded with KCO₃ so that the hot combustion gases at 2200°C are a conducting plasma. These gases move through the MHD generator, or so-called "channel", in which the positive and negative charges are bent toward opposite walls by a magnetic field, thereby setting up Hall voltages and currents. In present day designs the gases are still very hot when they leave the MHD generator so that they then are progressively cooled by producing steam for a conventional steam plant and by preheating the air for initial combustion.

It is clear that the materials of the combustor must operate above 2000°C in the presence of gases made up of oxygen, carbon and sulfur compounds. If coal is to be used there are additional chemical elements present, as for example Mg, Si and Fe from the coal slag. Also the potassium seed material is present, so that the life of combustor parts depends upon reaction rates and ion mobilities of a rather large variety of materials in the combustor. There have been few, if any, fundamental studies of material stability, diffusion, or mechanical property changes of insulators exposed to various ambients above 2000°C.

The temperature of gases at the surface of the MHD channel is somewhat lower than in the combustor. However, the structure of the channel is more complex. In the same way that the magnetic field causes perpendicular Hall currents, these Hall currents themselves produce longitudinal voltages, which require that the channel be built of alternating electrodes and insulators as shown in Fig. 5. Moreover, for a coal fired MHD plant slags will tend to settle as liquids and solids on the channel surfaces. Thus there will be solid-solid and solid-liquid interactions between the insulators, conducting electrodes and glassy or liquid slags. Clearly material compatibility, precipitation and phase boundary motion are important problems for basic study.

Large currents passing through the channel walls compound the difficulties. It is well known that ionic currents produce electrolysis and resultant changes of electrode bulk and surfaces. Very few studies of the effects of currents passing through refractory materials have been reported.

Table VI is a summary of the types of basic studies that would be helpful for designers of MHD generators. Also listed are some materials that are at present being discussed and tested for these very high temperature applications which involve electric fields and currents.

In summary then, the development of more efficient methods of transforming fossil and nuclear fuels into useful electricity requires a better understanding of ion mobility in refractory compounds. The techniques that have been used in the past to study ion mobility in alkali halides and metals need to be extended to the high melting oxides, carbides, and nitrides. Because of the high temperatures, the techniques used successfully near room temperature and at moderate temperatures in alkali halides cannot be applied without modification. In Table VII are listed some of the difficulties one might expect. These are respectively related to equipment (for example A) or multiple processes that

proceed simultaneously. Separating the multiple process will require keeping track not only of the parameter being varied deliberately, but also of seemingly irrelevant ones, as for example, sample history, sample chamber construction material, and ambient gases.

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Table I. Electricity Generation Technologies

Technology	Operating Temperatures	Solids Used	Degrading Atmospheres
Steam	600- 700	Steel Alloys	Steam
Aqueous Nuclear	500- 600	Steel Alloys	Water, Radiation
Gas Turbines	700- 900	Steel Alloys	O, C, S
<hr/>			
Advanced Nuclear	700-7100	Steel Alloys Oxide Fuels	Na, K, Fission Products, Radiation
Advanced Turbines	1500- (?)	Ceramics (?)	O, C, S
Thermonuclear	1000- (?)	(?)	H, Li, Radiation, Electric, Magnetic Fields
Magnetohydrodynamic	1700-2000	Ceramics	C, S, K, Si, O, Electric Fields and Currents

Table II. Melting Temperatures of Some Refractory Materials

TaC	3880	ZrN	2980	[UC	2450]
C	3650	Ti B ₂	2980	Y ₂ O ₃	2410
ZrC	3540	Ti N	2930	Ir	2410
N6C	3500	Nb B ₂	2900	B	2300
W	3410	W B ₂	2900	Cr ₂ O ₃	2265
Ta ₂ N	3360	WC	2870	Al N	2200
[ThO ₂	3300]	VC	2830	MgAl ₂ O ₄	2150
TiC	3160	[MgO	2800]	VB	2100
ZrB ₂	3040	[Si C	2700]	VN	2050
BN	3000	[ZrO ₂	2700]	W Si	2050
TaB ₂	3000	Mo C	2690	Al ₂ O ₃	2050]
Ta	3000	UN	2630	MgS	2000
		ThN	2625	NiO	1900]
		CeO ₂	2600	Mg ₂ SiO ₄	1910
		NbN	2575	Si ₃ N ₄	1900
		[CaZrO ₃	2550]		
		BeO ₂	2550		
		[UO ₂	2500]		

Table III. Basic Studies Needed for Advanced Nuclear Technology

1. Self Diffusion in UO_2 , UC , ThO_2 , ThC (also Ionic Conductivity).
 2. Diffusion of Cs , Sr (and other fission products) in Reactor Fuels.
 3. Grain Boundary and Gas Phase Transport.
 4. Aggregation, Nucleation and Growth.
 5. Radiation Enhanced Diffusion.
 6. Temperature Gradient Enhanced Diffusion.
-

Table IV. Basic Studies Needed for Advanced Gas Turbine Technology

1. Diffusion of C , S , in SiC , Si_3N_4 , SiO_2 .
2. Effect of Grain Boundaries, Glassy State on Ion Mobility and Mechanical Properties.
3. Kinetics of SiO_2 Film Growth on SiC , Si_3N_4 and Dependence on Ambient Atmosphere.
4. Effect of Temperature Gradient and Changes of Temperature on:
 - a) Reactions Between Si Compounds.
 - b) Stability of SiO_2 Film.
 - c) Mechanical Properties.

Table V. CTR Electrical Insulator Applications

	Mirror	Tokamak
Neutral Beam Injector Insulators	X	X
Direct Conversion Insulators	X	
Insulating Torus Ring		X
Low Z First Wall Liner		X
Loss Suppressing Blanket Insulators	X	X

Table VI. Basic Studies and Material for Magnetohydrodynamic Electricity Generation

Experiments

1. Diffusion of O, C, S, Si, Fe, K in Refractory Materials
2. Grain Boundary and Gas Phase Transport
3. Transport Number Determination
4. Effect of Electric Field on Ion Mobility
5. Effect of Trace Impurities on:
 - a) Electrical and Mechanical Breakdown Via Bulk or Boundaries
 - b) Ionic Conductivity
 - c) Electron Conductivity and Transport Number
 - d) Surface Reactions

Materials of Immediate Interest

Mg O

ZrO₂: Ca

MgAl₂O₄

MgFe₂O₄

} Spinel System

Al₂O₃

Mg₂SiO₄

Table VII. Difficulties Connected with High Temperature Materials Research

A. High Temperature Limits of Furnace

- 1) Furnace Heating Elements
- 2) Sample Chamber Tubes

B. High Vapor Pressure

- 1) Sample Contamination
- 2) Vacuum Difficult to Achieve
- 3) Materials Evaporate

C. Materials are Ionic/Covalent Compounds

- 1) Stoichiometry Depends on Ambient
- 2) Impurity Valence Can Change
- 3) Mixed Conductivity

D. Sample Preparation

No containment for Crystal Growth or Purification

FIGURE CAPTIONS

- Fig. 1. Logarithmic Plot of World Power Consumption vs Calendar Year.
- Fig. 2. Cross Sectional View of Two Types of Fuel Particles for Gas Cooled Reactors.
- Fig. 3. Cross Sectional View of Two Fuel Particles That Have been Irradiated in a Gas Cooled Reactor. The one with the UO_2 core shows thermomigration that is sufficient to breach containment.
- Fig. 4. Schematic Diagram of an Open Cycle Magnetohydrodynamic Generating Plant.
- Fig. 5. Cross Section of Channel Surface Showing Electrodes, Insulators and Slag Deposit. On the right is indicated the temperature to be expected across the channel surface for operating conditions.

WORLD POWER CONSUMPTION (equivalent metric tons of coal)

Fig. 1

OUTER ISOTROPIC
PYROLYTIC CARBON

SILICON CARBIDE
BARRIER COATING

INNER ISOTROPIC
PYROLYTIC CARBON

BUFFER
PYROLYTIC CARBON

Fig. 2

Y-12090C

Fig. 3

Schematic MHD Generator.

Fig. 4

ORNL-DWG 76-8209

Electrode-Insulator Cross-Section.

Fig. 5