Platinum-Clad Electrodes for Magnetohydrodynamic Generators

INDICATED LIFETIME WOULD AID COMMERCIALISATION

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The combination of a coal fired magnetohydrodynamic generator and a conventional steam-driven turbo-generator promises greater efficiency, cheaper electricity and lower environmental pollution than conventional power stations. Until recently, the unacceptably short lifetime of the anode electrodes has prevented this promise being fulfilled. Based upon tests described in this paper, it is predicted that the use of platinum-clad electrodes will dramatically increase the expected generator lifetime, thus paving the way to the commercialisation of magnetohydrodynamic energy converters. Approximately 1300 hours of electrode operation has now been achieved and an extrapolation of the results suggests a lifetime of 6000 to 8000 hours.

The principle of operation of a magnetohydrodynamic (MHD) generator is elegantly and deceptively simple. An electrically conductive gas, liquid or a combination of both is forced to flow through an applied magnetic field, which produces electromagnetic induction according to Ohm's law. The concept was first demonstrated by Michael Faraday in 1832 in an experiment conducted near Waterloo Bridge over the river Thames in London, England. Faraday submerged two copper plates connected by a wire on the opposite sides of the river and observed a slight electric current flowing through the wire. The expression below is a simplified form of Ohm's law which explains what occurred in the river:

$$J \approx \sigma (E + uB)$$

where J is the induced electric current density within the water, σ is the electrical conductivity of the river moving with velocity u, B is the earth's magnetic field and E represents the induced electric field. The same law is of course applicable to any kinetic to electrical energy conversion method. Early electricity generators used large piston engines to rotate solid copper conductors through a magnetic field and later the technology was improved by using turbines to rotate the conductors. However, in a MHD generator it is not a solid metal conductor but a gaseous conductor—in fact a high temperature ionised gas—that passes across the magnetic field created by a powerful magnet.

There are many different MHD generator geometries and many different working fluids (1). The first successful generator was built by R. J. Rosa at Avco Everett Research Laboratory in 1959 (2). It produced about 11kW and used argon as the working fluid. For a variety of reasons, most MHD research being carried out in the United States of America at the present time concentrates on linear generators with the combustion products of coal as the working fluid, the electrical conductivity of which is enhanced by the addition of potassium carbonate "seed". A typical coal-fired, commercially viable MHD generator converts about 20 per cent of the thermal input power to direct current electricity. Hence, at the exit of the generator most of the thermal energy is still in the gas but it is no longer usable for MHD power production due to its low electrical conductivity. However it is more

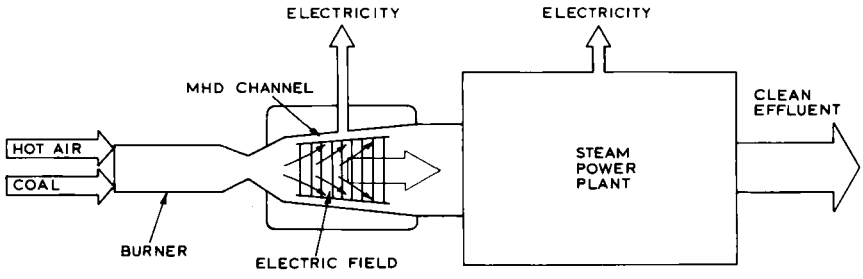

Fig. 1 Coal is burned in a combustor to produce an electrically conducting gas which passes through the magnetic field in the MHD section to generate electric power. The remaining heat is then used to operate a steam turbine, which produces additional electricity in a conventional way

than adequate to produce steam which is then used to power conventional turbo-generators. The combined MHD/steam cycle, shown in Figure 1, is thermodynamically in series and electrically in parallel. It has a potential for converting up to 60 per cent of the coal's energy into electricity, compared with 35 to 40 per cent for a conventional power plant. In addition the MHD generator removes most of the sulphur from the effluent due to a sulphur/potassium reaction inherent in the process, while at the same time nitrogen oxides are reduced to a level significantly lower than the U.S. Environmental Protection Agency's New Source Performance Standard (NSPS). Furthermore, the requirement for cooling water at a MHD power plant would be considerably less than that of a conventional power station, leading to reduced thermal pollution. The economic and some of the environmental advantages of a combined MHD/steam power plant over a conventional steam-only-plant are shown in Figures 2 and 3, respectively.

Because of its promise, MHD has been the

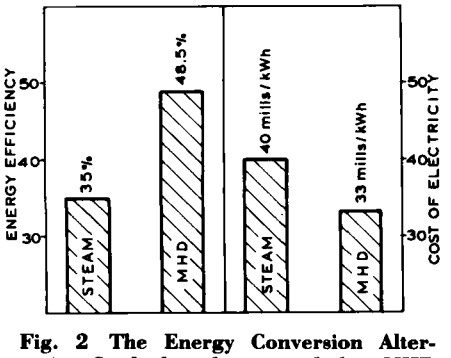

Fig. 2 The Energy Conversion Alternative Study has determined that MHD power plants will give higher operating efficiencies and cheaper electricity than modern base load steam plants (6). A combined MHD/steam bottoming cycle plant will be capable of producing 50 per cent more power from a given amount of coal than a modern steam plant (1 mill = 0.001 U.S. dollar)

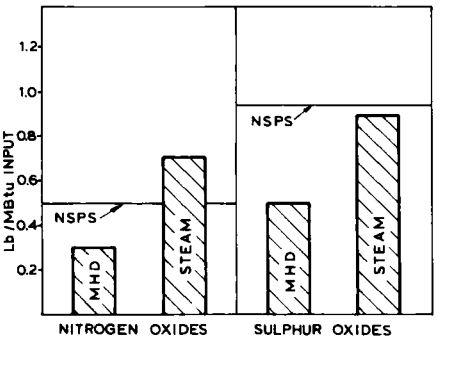

Fig. 3 The sulphur oxides and nitrogen oxides produced in a MHD plant will be appreciably less than those produced in a modern steam plant of the same power generating capacity and will be well below the U.S. Environmental Protection Agency's New Source Performance Standard (NSPS)

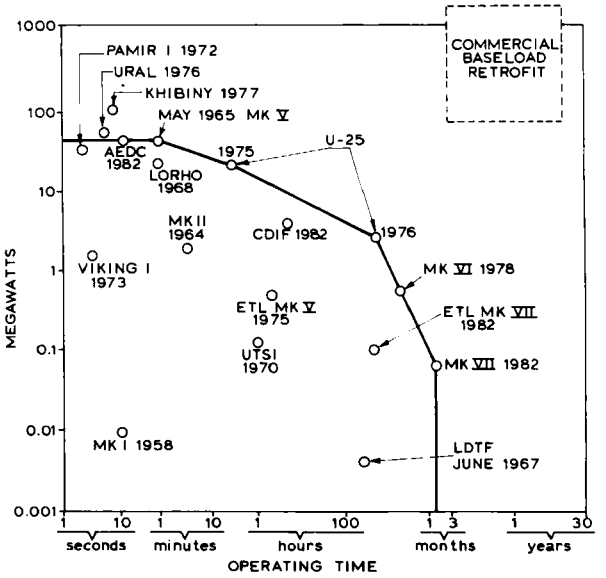

Fig. 4 This map of achieved power output and operating times demonstrates the progress made in MHD technology. For commercial viability the performance would have to fall within the indicated target area.

MK I, MK II, MK V, MK VI, MK VII, LDTE, VIKING, Avco Everett Research Laboratory Inc. (AERL Inc.) Everett, Massachusetts, U.S.A.

LORHO, Tested at Arnold Engineering Development Center, Tennessee, U.S.A. Designed and built by AERL Inc.

CDIF, Tested at Component Development and Integration Facility, Butte, Montana, U.S.A. Built by AERL Inc.

ETL MK V, ETL MK VII, Electrotechnical Laboratory, Ibaraki, Japan. PAMIR 1, URAL, KHIBINY, Portable fired by solid fuel rocket, U.S.S.R. U25, High Temperature Institute, Moscow, U.S.S.R. UTSI, University of Tennessee Space Institute, Tullahoma, U.S.A. AEDC, Arnold Engineering Developing Center, Tennessee, U.S.A.

subject of active research for almost three decades in many countries all over the world (3). The efforts intensified in the early seventies and since that time many problems which then seemed insurmountable have been solved.

The chosen strategy, illustrated in Figure 4, was to follow what became known as the two axis approach. Briefly stated this meant performing two types of experiments: the first, high power but short duration experiments aimed at investigating flow and plasma effects, and the second, small, lower power experiments aimed at investigating channel life-limiting effects. This dual approach reduced developmental risk and was less expensive than a programme that addressed all the issues in one experiment. Figure 4 identifies the boundaries of progress achieved to date. While raising the power boundary was not hard to achieve, extending the lifetime boundary was very difficult due to the extremely harsh operating environment in the generator channel.

Currently the Soviet Union is the closest to commercial MHD generation. A 500 MW MHD plant is being constructed about 100 miles east of Moscow. Several other countries including the U.S.A. are considering the so-called MHD Retrofit, which is the addition of a MHD topping cycle to an existing conventional steam plant.

A typical commercially viable coal-fired MHD generator, shown schematically in Figure 5, may be 10 to 20 metres long, with a 1 m^2 flow cross-section and will have hundreds of pairs of current collecting electrodes. The generator walls are subjected to a heat flux reaching 400 W/cm^2, to corrosion/erosion resulting from the hot (2500 K) high speed (1000 m/s) slag, sulphur and potassium laden gas flow, and also to electric fields that locally reach 10 kV/m. About 50 per cent of the internal surface of the generator is formed by electrodes, shown in Figure 6. Their operating conditions are further complicated by the

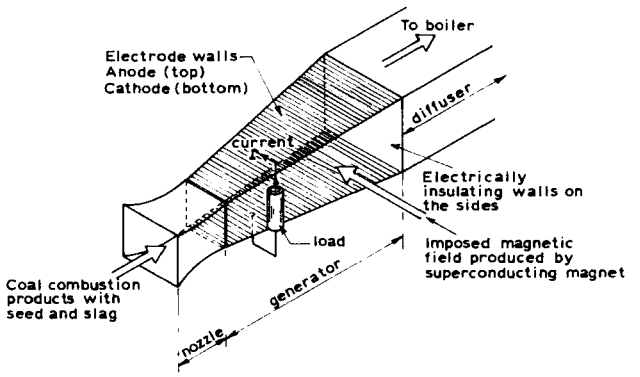

Fig. 5 A typical coal fired MHD generator could be 10 to 20 metres long and contain hundreds of pairs of electrodes. The electrically conducting gas produced by the combustion of coal enters the MHD generator at 3000 K, 10 atmospheres of pressure and a speed of 1000 metres per second; it leaves for the steam boiler at 2400 K and 1 atmosphere

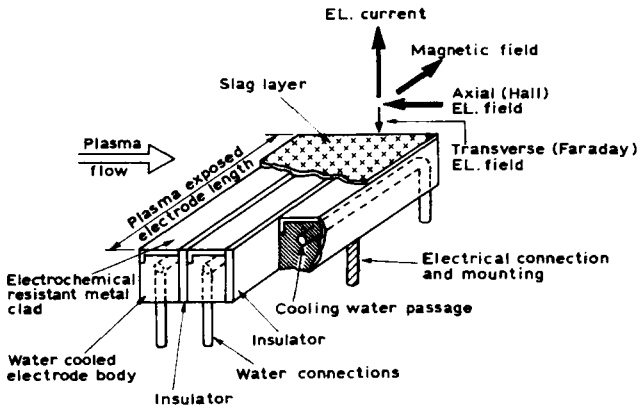

Fig. 6 Only three anodes are shown in this assembly but hundreds would be required in a commercial MHD generator. The upstream edge of each water cooled electrode is protected by an electrochemical resistant metal cladding and the electrodes are separated by boron nitride insulators

transport of current which can be either diffused or constricted (arcing). Of the two types of electrodes, namely anodes and cathodes (defined as electron emitters), the anodes have proved to be the life-limiting component of the generator and a major design challenge.

Anode Development

Severe corrosion is caused by the electrochemical attack on anode surfaces by negatively charged ions of oxygen and sulphur oxide radicals. These ions are liberated from the coal slag by arc current transport through the slag layer, and are driven to the anode surface by the electric field. Oxidation and sulphidation of the anodic surfaces, along with arc melting, were the major barriers to the development of long duration electrodes.

Early electrode designs consisted of various configurations of castable ceramics in metallic holders. To keep the ceramic hot and to reduce boundary layer joule dissipation, the gas-side metal surfaces operated at high temperatures and served as the current lead-out. Electrode voltage drop and heat transfer losses were minimised with this design. However, rapid oxidation of the metallic holders and slag fluxing of the ceramic resulted in short lifetimes. In order to achieve the durations required for central power stations, electrode designs evolved to progressively colder metal temperatures and minimal ceramic surfaces consistent with the development and retention of a continuous slag layer.

In 1978 a significant milestone was achieved. A 500 hour test had been undertaken in two

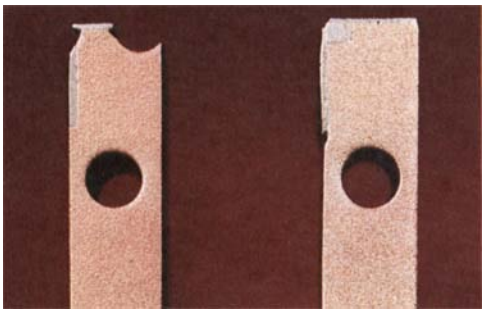

Fig. 7 In 1978 a significant improvement in anode life was achieved by cladding the upstream edge and anodic surfaces with platinum. These results of a 250 hour test show that the electrode erosion suffered by the earlier design of anode (left) was avoided on the platinum clad modification (right). Plasma flow is left to right

parts, with a complete tear-down inspection at the 250 hour midpoint. At this inspection the weak points of each electrode design were fairly obvious. Clearly the nickel alloy cladding used for anodic protection in the interelectrode gaps did not have sufficient oxidation resistance. Design modifications were therefore made to a small number of anodes and cathodes which were then incorporated in the second 250 hour test segment. The modified anodes used 0.010 inch thick platinum cladding on anodic surfaces and the upstream corner was reinforced with a 0.62 inch square platinum bar. Comparison of the 250 hour corrosion results for the initial and the modified designs are shown in Figure 7. A dramatic improvement is clearly evident in the platinum modified design.

Neither of these duration tests was made with sulphur in the plasma, which would be the case with coal combustion. Therefore a series of shorter duration tests (30 to 50 hours) were then conducted using sulphur additions, in amounts similar to those present in the combustion products of typical coals, with sulphur contents of 0.5 and 5 per cent, simulating Montana Rosebud and Illinois No. 6 coals, respectively. In the search for electrodes and in particular anodes, with adequate reliability and durability to satisfy the requirements of commercial operation a large number of configurations and candidate materials were evaluated. The noble metals tested for use as cladding materials were platinum, platinum-rhodium-iridium alloys, palladium and gold. The following basic electrode design criteria were established:

[i] A massive, well-cooled electrode body of high thermal diffusivity (copper) to retard electrolytic activity and quench electric arcs;

[ii] Anodic surfaces protected with a thin cladding of oxidation- and sulphur-resistant material;

[iii] Well-cooled inter-electrode insulators of good thermal conductivity to reduce current leakage and/or voltage breakdown;

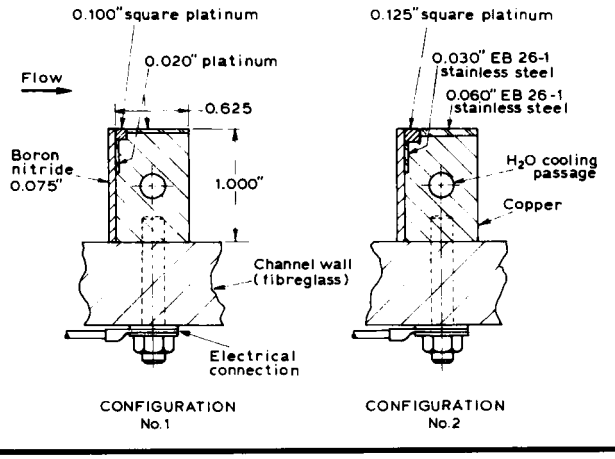

Fig. 8 Two configurations of MHD anode design have recently been tested for over 1000 hours in the Avco Mark VII power train. The water cooled copper electrodes are protected from oxidation and sulphidation by platinum in configuration No. 1 and by platinum plus stainless steel in configuration No. 2

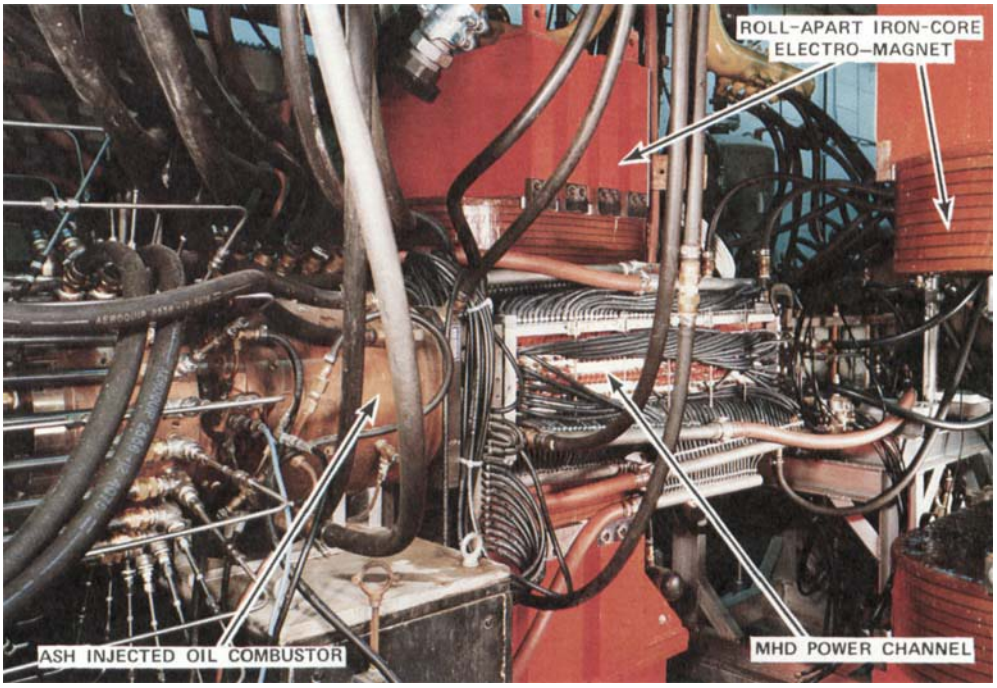

Fig. 9 The major components of the Avco Mark VII MHD power train are indicated, the 56 pairs of electrodes being located within the one metre long channel which produces a nominal 55kW

[iv] A slag-covered surface to protect the metallic electrodes from mechanical erosion by particle impact and to reduce their operating temperature as well as to minimise heat loss to the cooling water.

Various anode designs meeting these criteria were recently tested for over 1000 hours of operation (4). Two of the most successful configurations are shown in Figure 8. These represent the current state-of-the-art anode design, and are made of water-cooled copper with oxidation and sulphur-resistant cladding attached. Both designs have the upstream edges reinforced with platinum because the axial Hall field produces current concentrations along this edge. In configuration No. 1 the remainder of the anodic surfaces are clad with platinum foil while in configuration No. 2 a nickel-free stainless steel is used. The other anodes tested were variations of these two primary designs and cladding was accomplished by vacuum furnace brazing with a gold-nickel alloy.

The 1000 hour test was performed in the Avco Everett facility shown in Figure 9. Coal combustion was simulated by injecting fly ash and sulphur dioxide into the oil-fired combustor, the weight fraction of sulphur being 0.18 per cent of the total mass flow. The generator is one metre long and has 56 pairs of electrodes. Figure 10 shows the averages of current density, Hall (axial) electric field and electrical power density as a function of electrode number. The locations of the two primary anode configurations (Figure 8) are also shown.

Results and Discussion

Upon completion of the test, visual observations and a complete photographic record were made of each channel wall. The walls were carefully cleaned of attached slag and dismantled for individual weight measurements and photographic documentation. Slag samples were subjected to detailed analysis.

The general appearance of the anodes after the 1000 hour test was excellent. Figures 11 and 12 show the post-test condition of anodes of

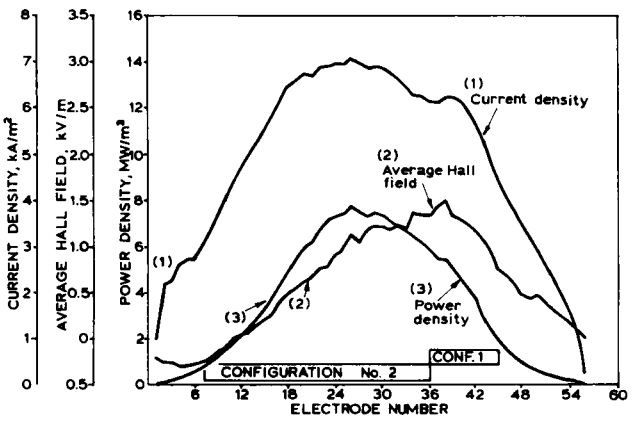

Fig. 10 The positions at which the two designs of electrode were used are shown here, together with the three average electrical parameters generated during the 1000 hour duration test

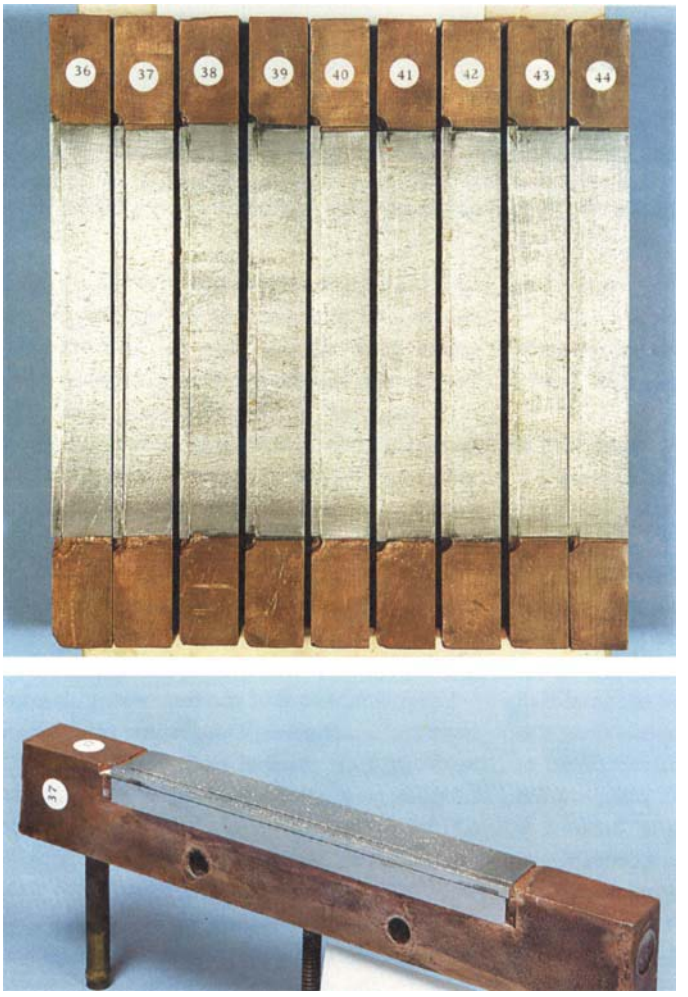

Fig. 11 Magnetohydrodynamic anodes of configuration No. 1 after 100 hours of power generation show that protecting the leading edge and the anodic surfaces with platinum has reduced erosion/corrosion of the anode to levels which suggest that platinum clad anodes could be used under the particularly harsh conditions prevailing in the first (upstream) third of a MHD channel (plasma flowing left to right)

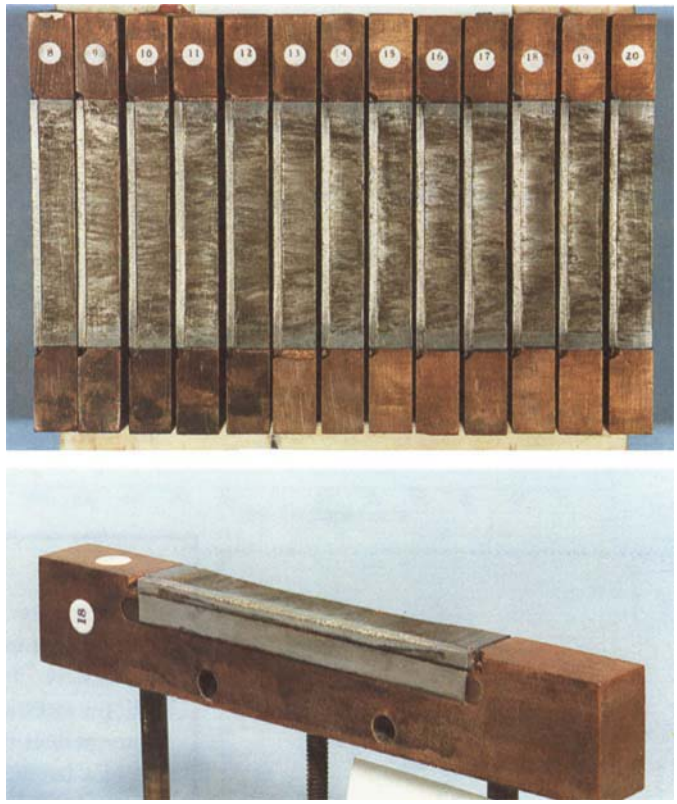

Fig. 12 After tests lasting 100 hours the satisfactory condition of these platinum and stainless steel clad anodes of configuration No. 2 enabled testing to continue. On the basis of present results it is suggested that this configuration of anode could be used in the middle third of a commercial MHD channel

design configurations No. 1 and No. 2 after removal of the slag layer.

Each anode was weighed at the start of the test, after 500 hours and at the completion of 1000 power hours. The mass loss for all the electrodes in the channel is given in Figure 13. Except for the extreme ends of the generator—Electrodes 1 to 7 and 46 to 56—the loss distribution resembles the current density profile shown in Figure 10. This indicates that the primary variable is the total charge that the electrode transports, as is shown by Figure 14. The slopes of the lines fitted through the two sets of data correspond to an erosion rate of 0.11 μg/coulomb for platinum electrodes and 0.24 μg/coulomb for the platinum/stainless steel electrodes. Furthermore the data indicate zero mass loss at zero current for the platinum electrodes but for the platinum/stainless steel electrodes there is a finite mass loss even at zero current. Thus it is evident that all, or nearly all of the platinum loss is due to electrical arcing or electrochemical attack whereas the stainless steel loss is partly mechanical and/or chemical erosion.

Detailed analysis of selected anodes suggests that the major cause of mass loss is melting and vaporisation caused by arcing. Figure 15, a scanning electron micrograph, shows an arc track on the surface of a platinum electrode (5), while Figure 16 shows the termination point of an arc on the platinum surface of the same electrode. Both clearly reveal melting. Further analysis of the surface of similar electrodes found no platinum/sulphur compounds (5). Thus all the evidence indicates melting and vaporisation to be the major cause of platinum loss. However other experiments suggest that the level of sulphur concentration does affect the rate of platinum loss, by reacting with locally molten metal.

Extrapolation of the 1000 hour erosion

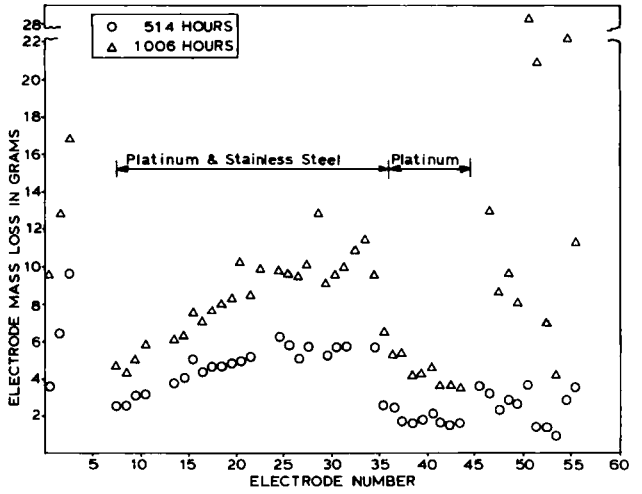

Fig. 13 Except for the two ends of the MHD channel, the mass loss distribution during the 1000 hour test resembles the current density profile, shown previously in Figure 10

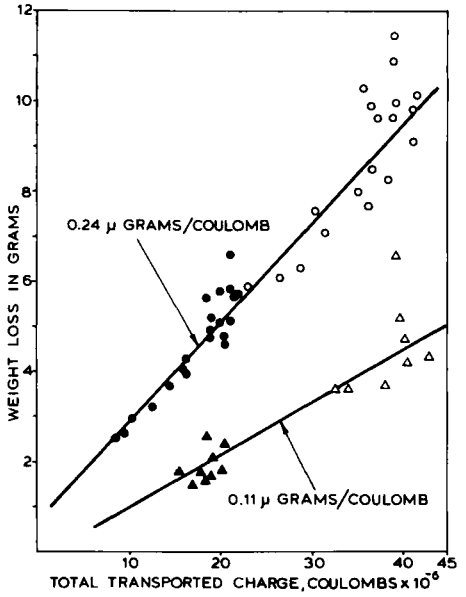

Fig. 14 These plots of mass loss versus electrical charge transported indicate that platinum clad anodes are eroded at a rate of 0.11μg/coulomb, while those protected by platinum and stainless steel lose metal at a rate of 0.24μg/coulomb

- ○ **platinum and stainless steel, configuration No. 2, at 1000 hours**
- • **platinum and stainless steel, configuration No. 2, 500 hours**
- △ **platinum and stainless steel, configuration No. 1, at 1000 hours**
- ▲ **platinum and stainless steel, configuration No. 1 at 500 hours**

measurements made on the platinum clad anode design indicates an electrode life of approximately 7500 hours. This assumes a uniform recession of the metal and is based on a current density of 0.6 A/cm^2. In an optimised 500 MW baseload MHD-steam power plant the MHD channel would have the following current density profile:

front third: 0.8 to 0.5 A/cm^2
middle third: 0.5 to 0.25 A/cm^2
rear third: 0.25 to 0.10 A/cm^2

thus, based on the recent test results, the recommended anode configurations to yield a life of 6000 to 7000 hours would be:

front third: platinum upstream corner + platinum anodic surface
middle third: platinum upstream corner + stainless steel anodic surface
rear third: stainless steel anodic surface.

The platinum required for the electrodes in a 500 MW generator would total 4500 troy ounces representing about 0.1 per cent of the world annual production and would cost around U.S. $1.2 million at today's prices. This represents less than 0.5 per cent of the estimated plant cost and would add at most 0.05 cents per kWh to the estimated cost of electricity. This cost could be reduced by reclaiming the platinum remaining on discarded

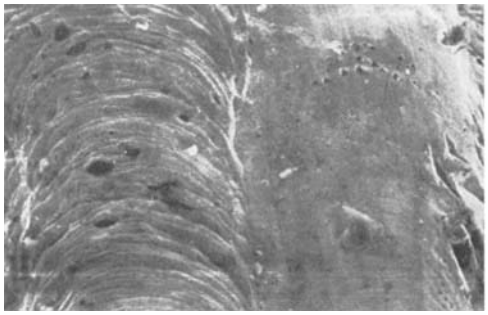

Fig. 15 This arc track across a platinum clad electrode surface, as seen under the scanning electron microscope, indicates melting of the platinum; the evidence suggests that melting and vaporisation are the major causes of platinum loss. The directions of plasma flow and arc movement are from top to bottom on the micrograph, which is reproduced here at a magnification of ×600 approximately. Reprinted from Reference (5)

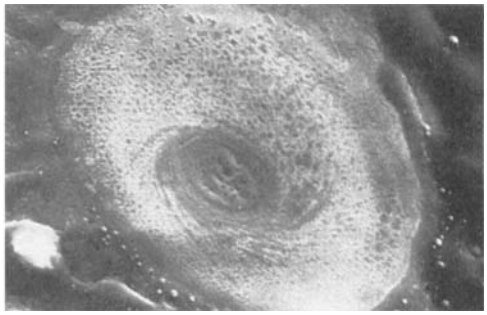

Fig. 16 An arc termination point on a platinum clad electrode surface again shows melting of the platinum, indicating that this is a cause of platinum loss during power generation. The magnification here is approximately ×1200. Reprinted from Reference (5)

electrodes or captured in the slag. However the amount is difficult to estimate, and therefore zero platinum recovery has been assumed. Thus neither the cost nor the availability would prevent the use of platinum for this potentially important application.

Testing anodes clad with platinum and with platinum plus stainless steel continues, with the objective to demonstrate 2000 operating hours. To date the electrodes have accumulated about 1300 hours. Basic studies of arcing and arc erosion on platinum electrodes are proceeding concurrently.

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Light-Assisted Oxidation of Cyanide Wastes

Many industrial processes including the case hardening of steel, electroplating and ore refining can result in waste waters that contain toxic concentrations of cyanide. These may be destroyed by alkaline chlorination or direct electrolytic oxidation, but the former produces considerable volumes of sludge for disposal while the latter incurs high energy costs.

However, recent work by C. E. Byvik of the National Aeronautics and Space Administration's Langley Research Center and A. Miles of Southern University has demonstrated another oxidation technique, and this is effective in reducing cyanide concentrations to levels which are significantly below those achieved by established methods ("Solar-Assisted Oxidation of Toxic Cyanide", LAR-13171/TN, *NTIS Tech. Notes*, October 1985).

In their solar-assisted oxidation technique, oxygen-containing air is bubbled through the waste cyanide solution, in which platinised titania powder is suspended, while it is subjected to either artificial or natural sunlight. The platinised semiconducting powders can be recovered and reused, and the results suggest that the process could become an effective and inexpensive method of treating cyanide-containing industrial waste water.