

ELECTROCHEMICAL ROUTE TO COAL GASIFICATION

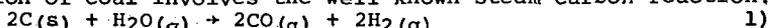
AND ITS TECHNOLOGICAL IMPLICATIONS

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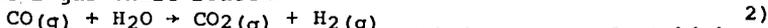
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Introduction

The production of synthetic natural gas or synthetic oil from coal consumes copious quantities of hydrogen that can be generated in large amounts only by processes which split the water molecule. Here we report on a new method for producing such hydrogen from coal, water and electric energy at mild temperatures. Conventional hydrothermal gasification of coal involves the well known steam-carbon reaction;

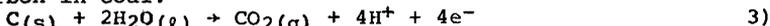


and the water gas shift reaction:

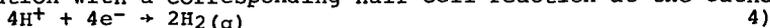


To ensure favorable equilibrium reaction 1) is conducted at high temperatures. The chemistry and technology of such coal gasification are complex and a detailed discussion of such matters, including hardware and gasification equipment, has been published by Squires [1] and others [2-3].

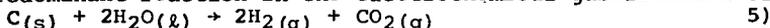
We have reported [4] a newly developed electrochemical process which converts coal and water into two separate gaseous products, the one comprising essentially gaseous oxides of carbon and the other essentially pure hydrogen. The process chemistry takes place at mild temperatures (even room temperature) and the gaseous products are essentially free of impurities such as ash, tar and sulfur compounds. This new electrochemical gasification process involves the anodic oxidation of coal at an electrode for which we postulate the half-cell reaction of the carbon in coal:



in combination with a corresponding half-cell reaction at the cathode:



The net sum of these half-cell reactions 3) and 4) is just the equation for the predominant reaction in the electrochemical gasification of coal:



The application of an electrical potential and the input of electrical energy overcomes the free-energy barrier for reaction 5) at low temperatures and permits it to be accomplished even at room temperatures and actual practical potentials of about 0.85V - 1.0V. The thermodynamic reversible potential ($|\Delta G|/nF$) for equation 5) at room temperature is only 0.21V. A notable advantage of electrochemical gasification of coal over conventional methods of coal gasification is the production of gaseous oxides of carbon at the anode and the simultaneous production of essentially pure hydrogen separately at the cathode. Because each gaseous product is produced separately and essentially free of impurities such as sulfur, tar and ash, subsequent cleaning, separation and purification steps are minimized. Other manuscripts [4,5,6] have introduced the process of electrochemical coal gasification and reported initial data as to the reactivities of various coals, the effect of different operating conditions and variables, and distinguished the process from conventional water electrolysis. Its relationship to conventional methods of coal gasification and the well known steam carbon reaction was also discussed. In the present paper we present results obtained in galvanostatic and potentiostatic studies, and we also consider the

technological implication of this process in the field of H₂ production, and electrowinning of metals from aqueous electrolytes.

Experimental

All experiments were conducted with stirred slurries of coal in aqueous electrolyte within the anode compartment of a cell (details of the experimental apparatus are given in references [4,5]). The external emf was applied by a potentiostat (both Model PAR 371 and PAR 179A were used) and the electrodes (both anode and cathode) were Pt mesh, gauge 52 (0.004" diameter wire) supplied by Mathey Bishop, Inc.

Potentiostatic Studies: Effect of Potential and Course of the Reaction

The higher the potential the greater the oxidation current. As the coal is consumed by oxidation at a given potential the current diminishes very slowly. This behavior is shown in Figure 1 where current is plotted vs. potential for various extents of coal consumption* as a parameter. Similar behavior is evident in Figure 2, where observed reaction rates of three different coal samples and one activated charcoal at 1.0V, using a coal slurry concentration of 0.069 gm/cm³ are plotted against cumulative coulombs passed. The results indicate that the rate of oxidation falls gradually as the reaction proceeds for all the samples studied. Only a portion (up to about 18% for NDL) of the coal can be consumed* before the rate of oxidation begins to fall steeply.

Previous workers [7-9] have reported that controlled oxidation of purer carbons, whether by electrochemical or chemical means results in the formation of several surface oxides. Of these oxides, the carboxylic group usually predominates. We believe, such oxides also form during the anodic oxidation of coal and they increase in concentration on the surface of the coal particles as the reaction advances, rendering electron abstraction more and more difficult, with consequent lowering of the oxidation current. Preliminary results obtained by analyzing the residual carbon values after partial electrochemical gasification of Pittsburgh coal also supports this view. Based on the known decomposition temperatures reported [10] for such surface oxygen compounds on carbon it should be possible to maintain a higher and steady oxidation rate at 200° - 600°C. It seems reasonable to consider surface oxides as intermediates in the pathway from coal and water as reactants to gaseous oxides of carbon and hydrogen as reaction products.

The decrease in oxidation current may also result in part from the accumulation on the coal particles of a tar-like coating that is formed during electrochemical coal gasification. Such a coating may be additional reaction products in the form of small aliphatic fragments which break away from larger coal molecules during anodic oxidation.

From Figure 2 it can be seen that the rate of oxidation of the Pittsburgh coal has dropped by a factor of about 7 when about 16% of the coal is electrochemically consumed. After it had been consumed to this extent, the coal was subjected to several treatments, to investigate the nature of the deactivation and explore the possibility of regeneration. The results disclose that the following treatments restore the original activity of the coal to a great extent: (A) washing with acetone which was also observed to remove tar-like material from the coal with the formation of a dark, perhaps colloidal, extract solution, and (B) heating in air to 250°C, which presumably removes accumulated

*Throughout this paper the extent of coal consumption is computed as the mass of carbon equivalent to total electrical charge passed during the experiment.

oxygen-containing surface functional groups [7]. In another experiment, North Dakota lignite was anodically oxidized at 1.0V and at 114°C with consumption of 26% of the coal, the remaining coal was filtered from the electrolyte, washed with acetone, and then heated in air to 250°C for 2 hours. This reactivated coal was then returned to the anolyte, and was further consumed an additional 20%. With the regenerated coal the oxidation current was almost equal to that observed with virgin coal and curve 2 of Figure 2 was essentially reproduced under the same conditions and with similar product formation. These experiments suggest that it would be possible to consume coal to a much larger extent at a meaningful rate by conducting the electrochemical gasification reaction at temperatures of about 200°C and above. Experiments at higher temperatures are planned and will be reported in another paper.

Galvanostatic Studies: Effect on the Cell Potential

North Dakota lignite was electrochemically gasified under galvanostatic conditions. Initially, the fresh coal samples were oxidized at a constant oxidation current of 150 mA until 9.82% of the coal was consumed, then the oxidation rate was lowered to 100 mA. The corresponding change of cell potential is plotted against the percentage of the total coal consumed in the process in Figure 3. The results clearly indicate that to maintain the desired rate of the reaction, the cell potential gradually rises because, as explained above, the coal particles become more and more unreactive as the reaction progresses (there may also be some effect due to decreasing coal concentration as well.) The potential required to maintain a constant current of 150 mA continues to rise in Figure 3 to about 1.2V (attained at first after about 97 hr) whereupon the required potential rises abruptly to about 1.7V, thereby suggesting the onset of a different reaction mechanism. As evident in Figure 3 this discontinuity at 1.2V was reproducible at two different currents (150mA and 100mA) and two corresponding different stages of coal consumption. It should be noted that analysis of the anode gas revealed only CO₂ and CO and no trace of O₂ until the potential reached 1.98V. It appears, therefore, that the discontinuity at 1.2V may correspond to the onset of a different mechanism of electrochemical coal gasification; it cannot be explained as the onset of simple water electrolysis.

Temperature Effects

It is suggested above that it would be possible to consume coal to a much larger extent at a meaningful rate by conducting the electrochemical gasification reaction at temperatures of about 200°C and above. Higher temperature operations may also provide other benefits:

- (i) polarization potentials (overvoltages) would be lowered and
- (ii) the reversible (thermodynamic) cell potential would also be lowered as explained below.

Figure 4 shows the effect of temperature on the reversible cell potential as computed from the thermodynamic ΔG and ΔH values of the electrochemical coal gasification reaction 5). Referring to this figure, the electrochemical coal gasification cannot occur below the reversible thermodynamic potential that corresponds to the Gibbs free energy of reaction (ΔG); this voltage decreases with increasing temperature. It is possible in principle for electrolysis to occur at any potential above the reversible thermodynamic value, if TAS is supplied as heat from the surroundings, but in practice polarization effects and other irreversibilities require larger potentials in order to operate at reasonable rates of reaction.

If the cell is operated at or above the thermoneutral voltage

($= \frac{|\Delta H|}{nF}$) both ΔG and $T\Delta S$ are supplied as electrical energy and no additional energy is required because the entire endothermic heat of reaction is supplied as electrical energy. Above the thermoneutral voltage there would be net heat generation and heat removal would be necessary.

Gases Produced and the Current Efficiency

During the oxidation of NDL, Pittsburgh coal, activated carbon and Montana Rosebud char at potentials between 0.8V to 1.2V the gas produced at the cathode was essentially pure H_2 and in each case the current efficiency of H_2 production was around 100% based on measured current integrated over time. The gas produced within the anode compartment was almost pure CO_2 with small amounts of CO. The composition of the anode gas, however, varies somewhat over the course of the gasification reaction; this may be attributed to corresponding changes in population of surface oxides on the coal. It is also observed that the volume ratio of the gases collected at the cathode to those at the anode ranged from about 9.1 to 3.7; the higher ratios were obtained at the beginning of the experiment but then decreased. According to the stoichiometry of reaction 5) this gas ratio should be about 2. Cathode-to-anode gas ratios greater than about 2.0 can be attributed mainly to accumulation of oxygen on the coal particles in the form of functional groups such as $-COOH$, $-CHO$, CH_2OH and the like. Moreover, higher relative amounts of H_2 may also be attributed in part as arising from the hydrogen content of the coal. Preliminary proximate analysis of the residual carbon after NDL gasification reveals preferential consumption of volatile components which are expected to be rich in hydrogen. The production of anode gas is probably strongly related to the concentration of the surface oxides of coal. Binder et al reported [7] that a surface layer forms first on graphite and only then does CO_2 evolution begin. As the oxidation process advance, surface oxides may build up to steady-state concentrations on the coal, whereupon the anode compartment gas generation rate becomes constant. A qualitative but sensitive mass spectrometric analysis was made of the gases produced at both anode and cathode. It is noteworthy that no lines were observed for molecular weights corresponding to SO_2 or H_2S --even though the parent coals contain significant sulfur.

Implications for Hydrogen Production

The more common approaches to splitting the water molecule to recover hydrogen have utilized either electrical energy alone or fossil fuel in combination with thermal energy. It appears that the production of hydrogen by the combined use of fossil fuel and electrical energy as we report has not previously been investigated or applied. In the following the efficiency of H_2 production by our new process ("Coal-Consuming Water Electrolysis") is compared with ordinary water electrolysis. In water electrolysis the energy required to split the water molecule is supplied solely by electricity, whereas in our new process the required energy is supplied only in part by electricity with the balance arising by way of the concomitant anodic oxidation of coal. The following quantitative development gives a first order approximation of how much energy comes from each such source and thereby provides a rough feeling for efficiency. The energy consumed by conventional water electrolysis conducted at a potential of E_2 to produce N_{H_2} moles of H_2 is $2N_{H_2} F E_2$ whereas the energy required by the present process under investigation operating at a potential of E is:

$$E \int_0^t i dt + N_c (-\Delta H) \quad (6)$$

where E is the potential applied across the cell, i is the current and

t is time. N_C is the number of moles of carbon consumed and ΔH is the enthalpy of combustion of carbon to CO_2 .

The foregoing expression can be simplified by assuming a constant operating potential E , and noting that:

$$N_{H_2} = \int i dt / 2F \quad 7)$$

$$\text{and } N_C = 1/2 N_{H_2} \quad 8)$$

where F , the Faraday constant, is 96,500 coulombs/equivalent.

Eliminating $\int i dt$ and N_C the expression for total energy consumption by our process becomes:

$$2FN_{H_2}E + 1/2 N_{H_2}(-\Delta H) \quad 9)$$

The relative energy usage (REU) is accordingly:

$$\text{REU} \left(\frac{\text{Ordinary Electrolysis}}{\text{Coal Assisted Electrolysis}} \right) = \frac{2N_{H_2}F E_2}{2F N_{H_2}E + 1/2 N_{H_2}|\Delta H|} \quad 10)$$

$$= E_2 / (E + |\Delta H|/4F)$$

Inserting $|\Delta H| = 94,100 \times 4.18$ joules/mole and the value of F gives:

$$\text{REU} = E_2 / (E + 1.02) \quad 11)$$

Practical values of E_2 for conventional electrolysis are about 1.8-2.0V whereas values of E observed in the present work have ranged from about 0.8 to about 1.0 volt at room temperature. This means that, per unit of hydrogen produced, the total energy consumption is about the same ($\text{REU} \approx 1$) for ordinary water electrolysis and for coal-assisted water electrolysis conducted in the experiments near room temperature reported here. In the case of electrochemical gasification to hydrogen, however, about half the required energy comes directly from coal and half from electricity. We expect that the total energy requirement for coal-assisted water electrolysis can be lowered further by conducting it at higher temperatures thereby permitting operation at lower potentials (E) than 0.8 - 1.0 volt. A detailed economic analysis reported elsewhere [5] shows that coal-assisted electrolysis has its most favorable effect when electricity costs are high because cheaper coal energy is substituted for more costly electrical energy. The greatest effect (a 27% reduction in hydrogen cost) is evident for application with SPE technology at "normal" power costs of \$0.027/kw.hr.: the corresponding cost reduction for conventional electrolysis is 18%. For off-peak power at \$0.01/kw.hr. it is seen that direct incorporation of coal into the electrolysis process seems to offer no particular advantage.

Implications for Electrowinning of Metals

Electrochemical coal gasification can be extended to the electrowinning of metals by substituting the half cell reaction 3) (which consumes coal) for the half-cell reaction of oxygen evolution which ordinarily takes place during conventional electrowinning of metals from aqueous solutions of their salts. By this coal-based innovation the total overall cell potential of the resulting metal electrowinning process is lowered by about 1.10V with a corresponding significant reduction in the consumption of electrical energy. As a test case Cu was deposited on a platinum mesh cathode (separated from the anode by a fritted glass barrier) from aqueous electrolyte (0.125 M $CuSO_4$ in 0.5 M H_2SO_4) at 60°C, at two different galvanostatic rates; 5.9 mA and 12 mA. The corresponding change in cell potential is plotted in Figure 5. It is evident that the conventional copper electrowinning

reactions took place at cell potentials of about 1.65V and 1.73V respectively. Also plotted in Figure 5 are the results obtained in parallel experiments conducted in identical fashion except that the coal was simultaneously oxidized at the anode according to equation 3) while Cu cations were reduced at the cathode. In these latter experiments, North Dakota lignite (NDL) coal slurry (0.15 gm/cm³) was introduced into the anode compartment of the cell and was anodically oxidized while copper deposited on the cathode under identical galvanostatic experimental conditions. As a result of the oxidation or gasification of the coal at the anode, the overall cell potential was lowered by about 1.1V, compared to the conventional process. This is evident from the comparative data plotted in Figure 5.

Concluding Remarks

It has been shown in this study that

- (i) different coals have different reactivities for electrochemical gasification and in each case the reactivity of the particular coal falls gradually as the reaction advances.
- (ii) the original reactivity of the coal samples can be restored by acetone washing and heating at temperatures between 200° - 600°C.
- (iii) high temperature operation promises several advantages.
- (iv) two different coal oxidation mechanisms appear to occur in two correspondingly different potential regions of oxidation.
- (v) hydrogen production and electrowinning of metals from aqueous electrolytes are the processes where electrochemical coal gasification may find application.

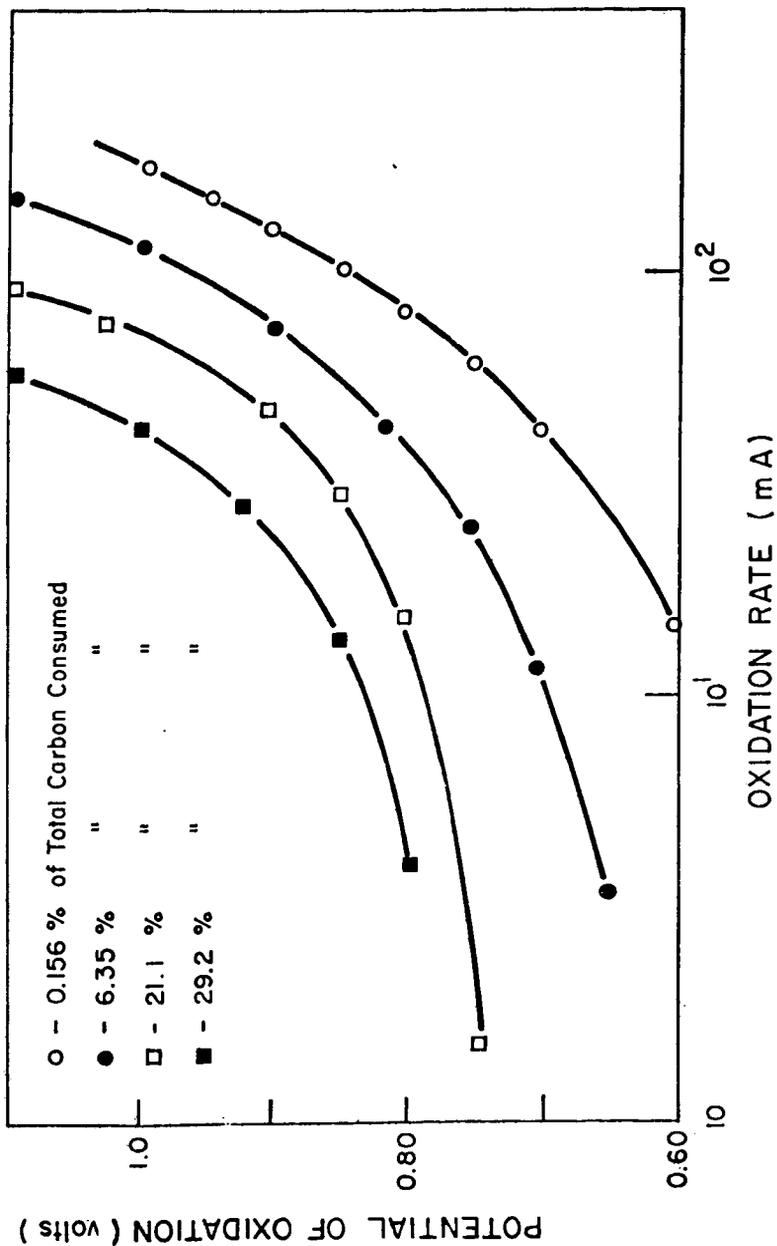
Mass balance calculations, high temperature reaction and use of anodes other than platinum are currently in progress.

Acknowledgement

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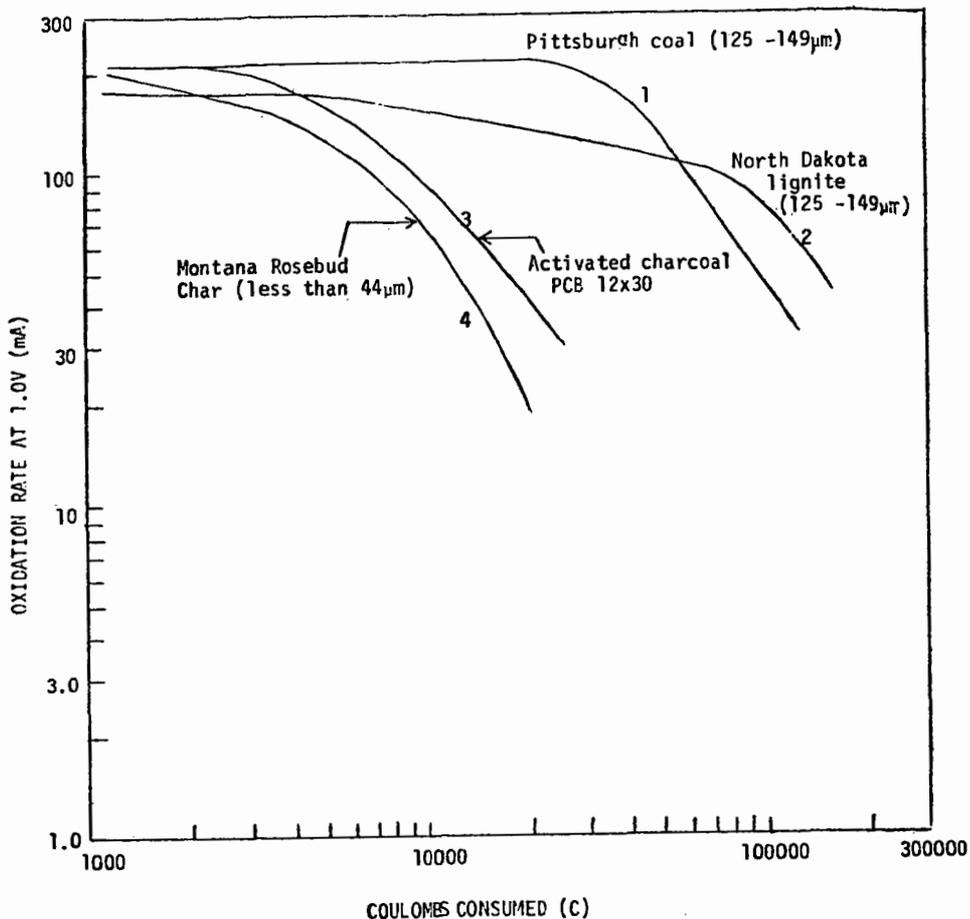
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1. Effect of Potential on the Oxidation Rate as the Reaction Proceeds.

(North Dakota Lignite; Coal Slurry Conc.: 0.069 gm/cm³; Supporting Electrolyte: 5.60 M H₂SO₄; Particle Size: 125 - 149μm, Temp. 114°C; Anode area: 96.5 cm² (geometrical)).



2. Oxidation Rate of Different Samples At 1.0V as the Reaction Proceeds •

(Slurry Conc.: 0.069 gm/cm³; Particle Size: 44µm and below;
 Electrolyte: 5.6M H₂SO₄; Potential: 1.0V; Anode area:
 96.5 cm² (geometrical); Temp. 114°C.

Electrolysis discontinued after:

- Curve 1: 343 hours and 16.36% consumed
- Curve 2: 353 hours and 29.2% consumed
- Curve 3: 110 hours and about 2.56% consumed
- Curve 4: 78 hours and 3.2% consumed

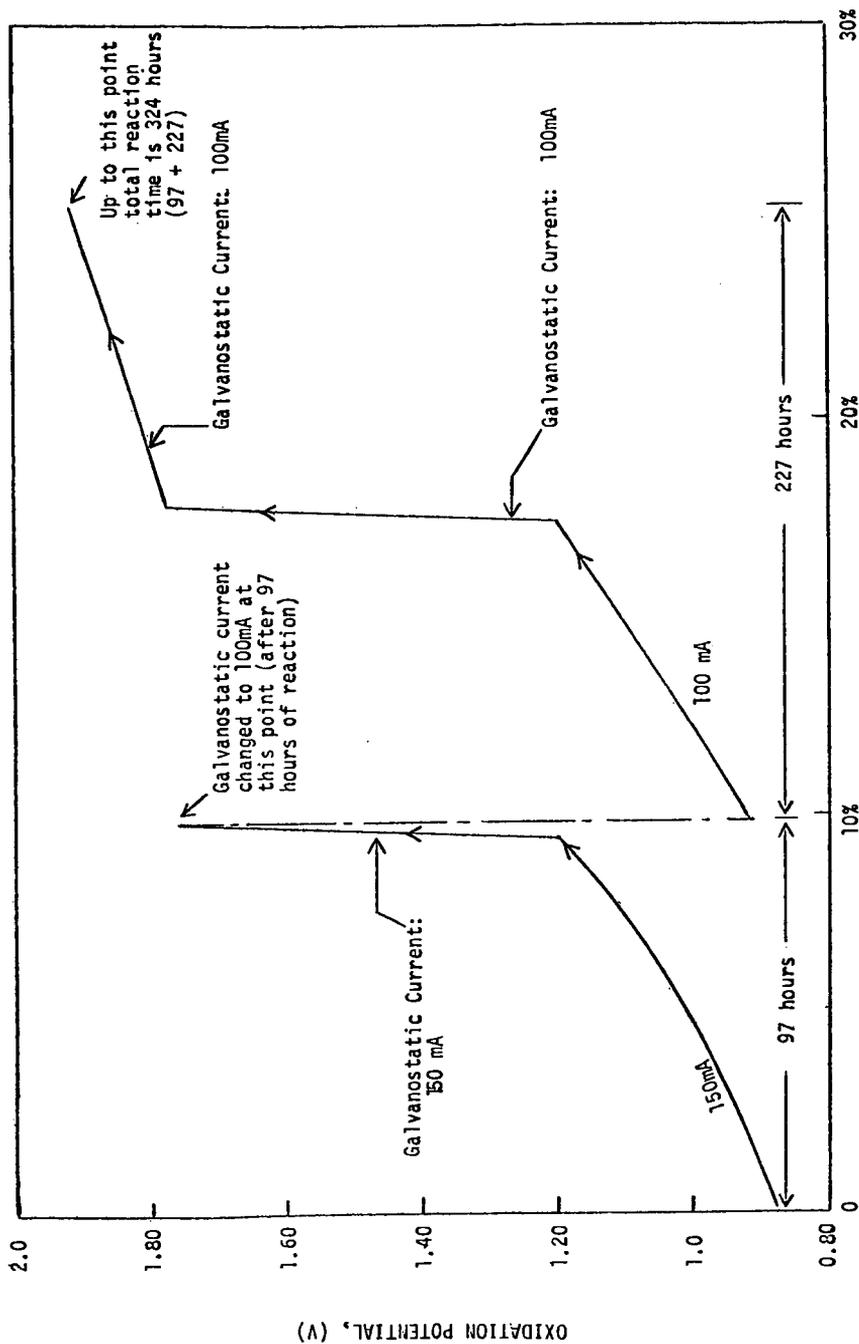


Figure 3. Change of Cell Potential During Galvanostatic Study.

(Coal sample: Fresh ND1; Slurry Conc.: 0.069 gm/cm³;
 Electrolyte: 5.6M H₂SO₄; Particle size: 105-125µm;
 Anode area: 96.5 cm² (geometrical).)

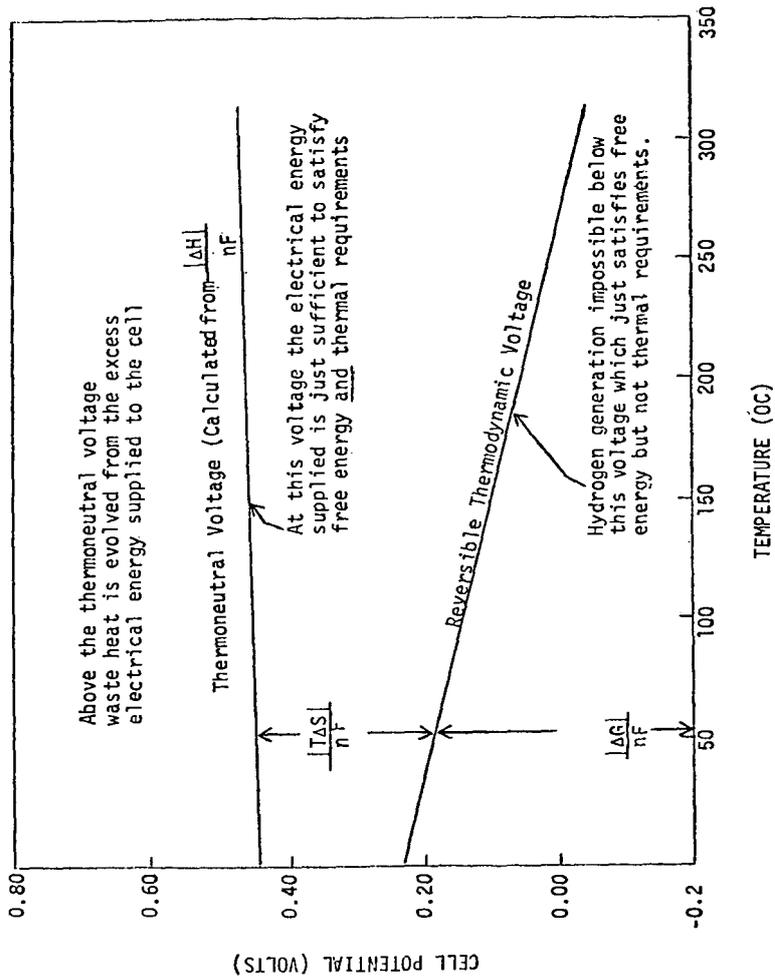


Figure 4. Effect of Operating Temperature on Cell Voltage.

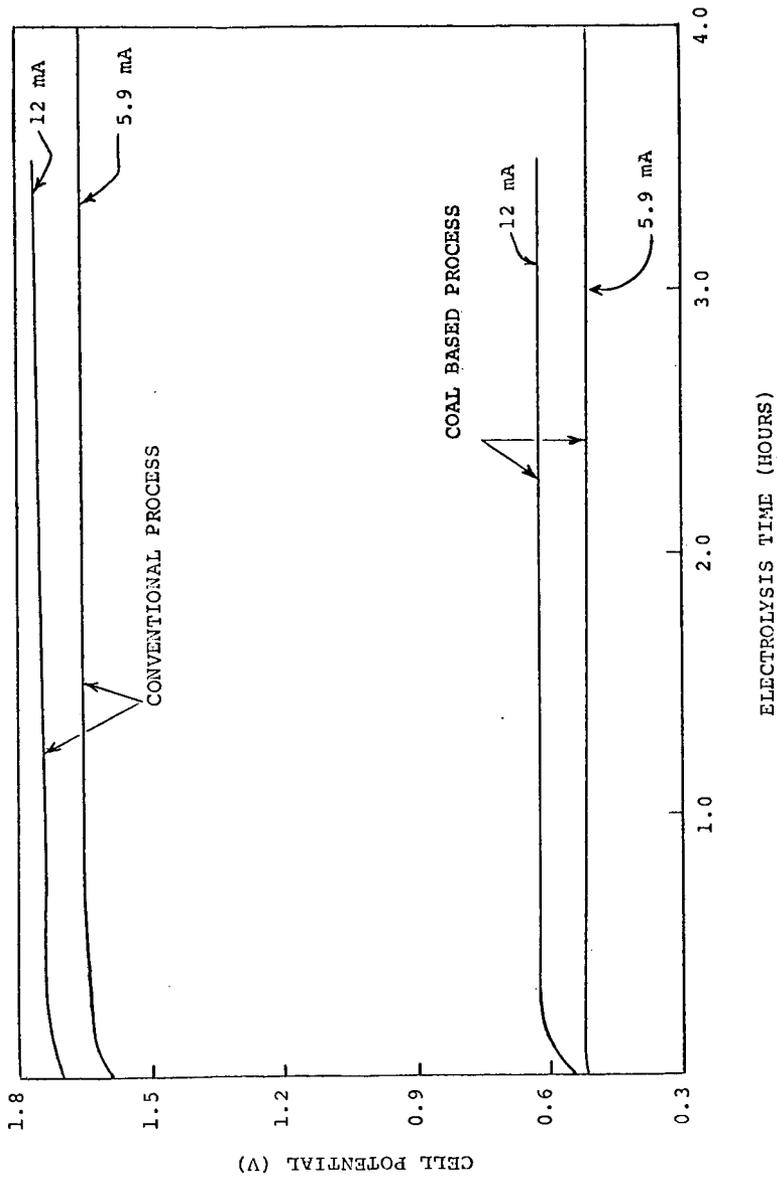


Figure 5. Comparison of the Cell Potentials of the Conventional and Coal Based Copper Electro-winning Processes .
 (Electrolyte: 0.125M CuSO₄ and 0.5M H₂SO₄; Coal Sample N. Dakota Lignite; Slurry Conc.: 0.15gm/cm³; Particle size: 74-88µm; Temp.: 60°C; Anode area: 5.3 cm² (geometrical).