

# The industrial application of a uranium dioxide electrode

by C. R. S. NEEDES\*, Ph.D. (London) (Visitor), M. J. NICOL†, Ph.D. (Rand) (Visitor),  
N. P. FINKELSTEIN† M.Sc. (Rhodes), Ph.D. (Liverpool) (Fellow), and  
G. T. W. ORMROD† (Visitor)

## SYNOPSIS

A correlation between the potential of a  $UO_2$  electrode and the rate of recovery of uranium has been proved in laboratory and plant trials. When the recovery rates change because of variation in the concentrations of  $Fe(III)$ ,  $Fe(II)$ ,  $SO_4^{2-}$  and  $H^+$ , a positive correlation is observed.

However, an increase in the concentration of phosphate in solution produces an increase in the  $UO_2$  electrode potential but a decrease in the rate of leaching of  $UO_2$ . The correlation between the  $UO_2$  electrode potential and the rate of leaching of  $UO_2$  is then negative.

It is concluded that, as a control device, the electrode cannot compete with the platinum electrode for use on certain plants. Nevertheless, the  $UO_2$  electrode will act as a useful warning device if the total concentration of iron in solution decreases to below a level concomitant with the economic recovery of uranium. Furthermore, because of the positive correlation between the  $UO_2$  electrode potential and the phosphate concentration, the electrode will also be of value in the detection of an increase in the phosphate level in solution.

When it was incorporated in a suitable industrial probe, the electrode was found to be able to withstand the rigours of the leaching conditions in a large pilot-plant pachuca, and only failed after six weeks' operation.

## SAMEVATTING

Daar is 'n korrelasie tussen die potensiaal van 'n  $UO_2$ -elektrode en die herwinningstempo van uraan in laboratorium- en aanlegtoetse bewys. Wanneer die herwinningstempo verander as gevolg van 'n variasie in die konsentrasie van  $Fe(III)$ ,  $Fe(II)$ ,  $SO_4^{2-}$ , en  $H^+$ , word daar 'n positiewe korrelasie waargeneem.

'n Verhoging van die fosfaat konsentrasie in oplossing veroorsaak egter 'n toename in die  $UO_2$ -elektrodepotensiaal maar 'n afname in die loogtempo van  $UO_2$ . Die korrelasie tussen die  $UO_2$ -elektrodepotensiaal en die loogtempo van  $UO_2$  is dan negatief.

Die gevolgtrekking word gemaak dat die elektrode as 'n kontroletoestel nie met die platinelektrode kan meeding nie vir sover dit gebruik by sekere aanlegginge betref. Nietemin sal die  $UO_2$ -elektrode as 'n nuttige waarskuwingstoestel dien wanneer die totale ysterkonsentrasie in oplossing daal tot 'n laer peil as wat met die ekonomiese herwinning van uraan gepaard gaan. Verder sal die elektrode vanwee die positiewe korrelasie tussen die  $UO_2$ -elektrodepotensiaal en die fosfaat konsentrasie ook van waarde wees by die waarneming van 'n toename in die fosfaatpeil in oplossing.

Toe dit in 'n geskikte industriële sonde ingesluit is, is daar gevind dat die elektrode die strawwe loogtoestande in 'n groot proefaanleg-pachuca kan weerstaan en dit het eers nadat dit ses maande lank in gebruik was, gefaal.

## INTRODUCTION

Studies of the electrochemical nature of the dissolution of synthetic uranium dioxide, which were conducted at the National Institute for Metallurgy<sup>1</sup>, demonstrated that the potential of a  $UO_2$  surface in contact with a leaching solution is related to the rate of leaching of  $UO_2$  in that medium. This was verified satisfactorily for a natural sample of uraninite.

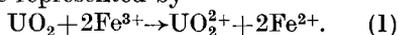
The importance of this correlation lies in the fact that the  $UO_2$  electrode could provide a useful tool for the control of commercial leaching operations. Therefore, a series of laboratory and plant tests were carried out so that the capability of the electrode in this function could be assessed.

\*Present address: E. I. Du Pont de Nemours, Wilmington, Delaware, U.S.A.  
†National Institute for Metallurgy, Johannesburg.

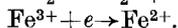
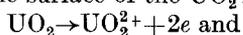
## THEORY OF THE OPERATION OF THE ELECTRODES

### The Uranium Dioxide Electrode

The overall reaction for the leaching of  $UO_2$  in the presence of an oxidant such as ferric ion can be represented by



This can be separated into two half-cell reactions, which are considered to occur simultaneously at the surface of the  $UO_2$ :



If these reactions are studied independently by simple electrochemical techniques, curves of stationary current density against potential (such as those designated *AB* and *CD* in Fig. 1) are obtained. Curve *AB* represents the anodic current flowing per unit area of  $UO_2$  surface at a potential *E*. If the current efficiency is assumed to be 100 per cent<sup>1, 2</sup>, the number of

gram-equivalents of uranium that dissolve over a specified period of time can be calculated from the laws of electrolysis. Similarly, curve *CD* represents the cathodic current flowing per unit area when the oxidant accepts electrons from the  $UO_2$  surface and is reduced. The chemical leaching of  $UO_2$  (equation 1) proceeds via the formation of electrochemical cells on the surface of the  $UO_2$ . The integrated internal current flowing from these cells corresponds to  $i_{AD}$ , which is the same as the external current flowing in the system when a potential  $E_{AD}$  is applied to an electrode immersed in a solution in which the oxidant is absent. This potential represents the 'mixed' potential of the oxidant- $UO_2$  system, and will be referred to in the following discussions as the  $UO_2$ -electrode potential.

If the concentration of the oxidant in solution is increased, the curve

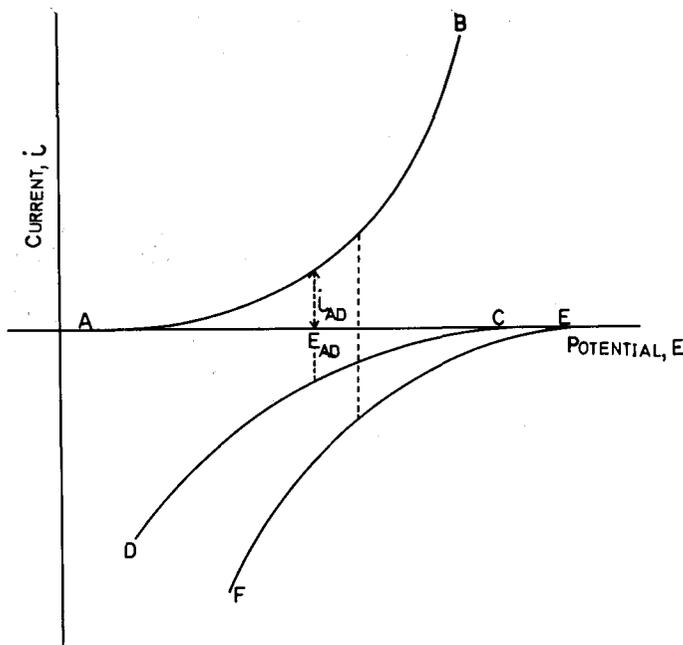


Fig. 1—Theory of the operation of the  $UO_2$  electrode. Current versus potential relationships for AB: the anodic dissolution of  $UO_2$ . CD, EF: the cathodic reduction of Fe(III) of different concentrations

of density against potential for the reduction of the oxidant at the  $UO_2$  surface shifts from CD to EF. Provided that the background medium is unchanged, the anodic oxidation current for  $UO_2$  increases with an increasing concentration of oxidant, and this is accompanied by a corresponding increase in the  $UO_2$ -electrode potential. In this particular instance, therefore, there is a positive correlation of the rate of leaching of  $UO_2$  with the potential of the  $UO_2$  surface in contact with the leaching medium. However, as will be demonstrated, the argument is complicated by the presence, in the background medium, of ions as  $H^+$ ,  $SO_4^{2+}$ , and  $PO_4^{3-}$ , all of which are important to the leaching of uranium. Although the rates of each of the two half-cell reactions above vary regularly with changes in concentrations of these ions, in some instances these changes are such that the resulting  $UO_2$ -electrode potential cannot be interpreted unambiguously in terms of the rate of dissolution of  $UO_2$ . Therefore, it was felt important to establish which of these effects would influence the performance of the electrode under plant conditions.

### The Platinum Electrode

The use of a platinum indicator electrode as a control element for the addition of manganese dioxide or other oxidants to the pachucas on uranium plants has been the subject of considerable investigation. The redox potential ( $E_{Pt}$ ) of the electrode in a pachuca depends essentially on the ratio of Fe(III) to Fe(II) in solution and is given by the Nernst equation

$$E_{Pt} = E^o - 0,059 \log$$

$$\left\{ \frac{[Fe(II)]}{[Fe(III)]} \right\} \text{ at } 25^\circ C,$$

where  $E^o$  is the formal potential (corresponding to the case  $[Fe(II)] = [Fe(III)]$ ) of the couple. This potential, therefore, is simply an indicator of the extent to which the iron in solution is oxidized, but, as will be discussed later, it will give no information regarding the total iron content of the solution.

### TESTWORK

The description and results of the testwork will be divided into three sections. The first involves

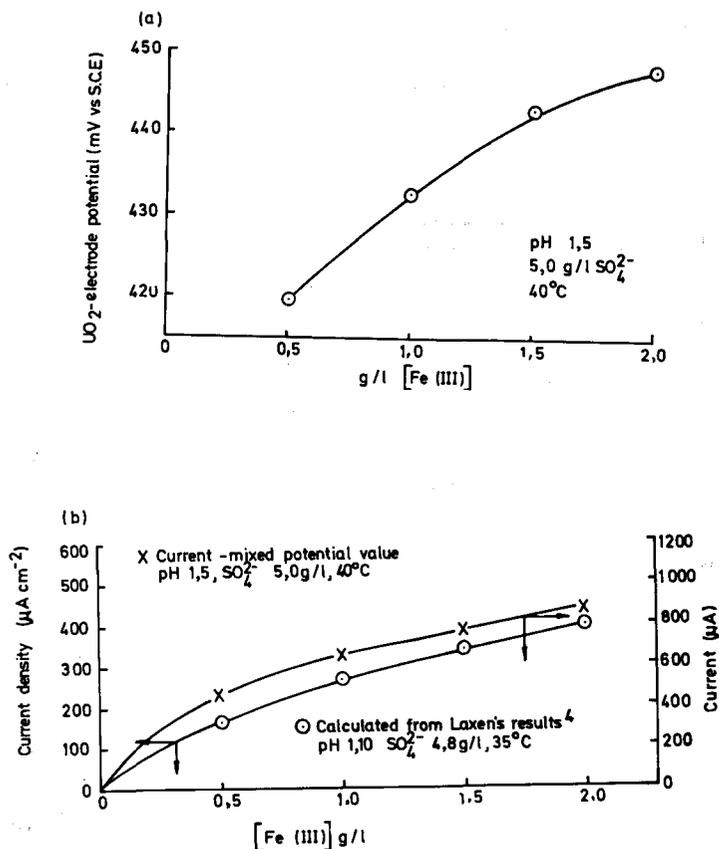


Fig. 2—Correlation between the  $UO_2$ -electrode potential, the current equivalent to the rate of leaching of  $UO_2$ , and the Fe(III) concentration

the leaching of pure  $\text{UO}_2$  in laboratory experiments designed to establish the factors that influence the performance of the electrode. The second describes similar experiments using ore samples, while the third describes the results obtained with the electrode on a large pilot plant.

### Construction of the Electrodes

Polycrystalline samples of  $\text{UO}_2$  were obtained from the South African Atomic Energy Board. A suitable piece was ground into a cylinder 1 cm in length and 0,5 cm in diameter, and one of the end faces was electroplated with copper. After a copper lead had been soldered to this end, the cylinder was mounted in a polypropylene capsule and sealed by being melted with a hot-air gun. In plant use, the capsule was then inserted, together with a platinum electrode of similar construction and a reference (Lazaran) electrode, into a special holder that has been described elsewhere<sup>3</sup>.

The Lazaran electrode is an industrial modification of the silver/silver chloride reference electrode and was preferred because of its robust construction, minimal maintenance requirements, and the ease with which it could be incorporated in the holder. Laboratory experiments were carried out with saturated calomel reference electrodes (S.C.E.) whose potential is 60 mV greater than that of the Lazaran electrode.

### Correlation of the Rate of Leaching with Electrode Potential

A number of leaching tests were carried out on the electrode so that the correlation of the  $\text{UO}_2$ -electrode potential with the rate of leaching of  $\text{UO}_2$  could be assessed without the complications afforded by the presence of an ore sample. Essentially, these tests consisted of the measurement of  $\text{UO}_2$ -electrode potentials in solutions similar to those encountered in practice, followed by the application of these potentials to a  $\text{UO}_2$  electrode immersed in the corresponding background electrolytes (i.e., in the absence of the oxidant), and the measurement of the currents flow-

ing. The trend in current values for changes in composition of solution is a measure of the trend in apparent leaching rates under the same conditions. Only apparent leaching rates can be quoted, since surface roughness and changing surface area rendered an absolute determination difficult.

### Variation of the Concentrations of Fe(III) and Fe(II)

Evidence of a positive correlation between the  $\text{UO}_2$ -electrode potential and the current measured at various concentrations of Fe(III) is given in Fig. 2. To confirm the trend of these values, some previous leaching results<sup>4</sup> (converted into current densities) are also presented. Fig. 3 shows that, although the  $\text{UO}_2$ -electrode potential responds to changes in the concentrations of Fe(III), the effect of Fe(II) is not apparent except at relatively high concentrations. The leaching rate, as measured by the current, follows a similar trend. From this, it can be concluded that the  $\text{UO}_2$  electrode will respond to the presence of Fe(II) only when the concentration is sufficient to affect the leaching rate. This point will be discussed in greater detail in a later section

when comparison is made with the platinum electrode.

### Variation of Sulphate Concentration, pH, and Phosphate Concentration

The data in Fig. 4 show that an increase in sulphate concentration at all concentrations of industrial interest leads to a decrease in both the  $\text{UO}_2$ -electrode potential and the rate of leaching. This decrease is a result of the fact that, at these concentrations, sulphate inhibits the cathodic reduction of Fe(III), presumably by formation of the less reactive  $\text{Fe}(\text{SO}_4)_2^-$  species<sup>5</sup>.

As indicated in Fig. 5(a), the relationship between the  $\text{UO}_2$ -electrode potential and pH is simple. However, because both the anodic and the cathodic components of the reaction vary with pH, the relationship between the  $\text{UO}_2$ -electrode potential, pH, and leaching rate is complex. For example, the anodic oxidation of  $\text{UO}_2$  is strongly influenced by pH and reaches a maximum<sup>2</sup> at a pH value of 2,0. Although the cathodic reduction of Fe(III) also varies with pH and achieves a flat maximum<sup>5</sup> at a pH value of 1,5, the former is the dominant effect. This is borne out by the results of Fig. 5(b), which

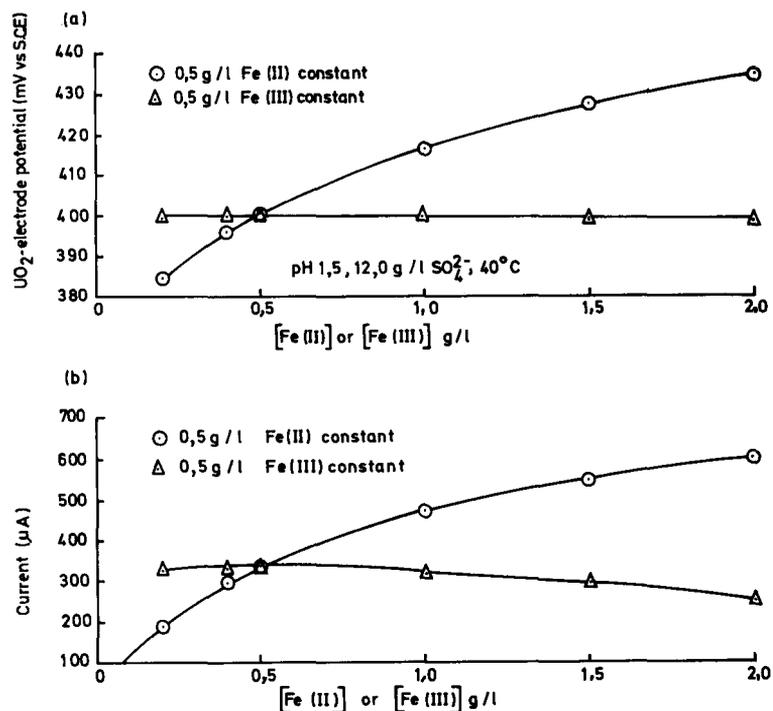


Fig. 3—A demonstration of the effect of Fe(II) on the current equivalent to the rate of leaching of  $\text{UO}_2$ , and on the corresponding correlation with the  $\text{UO}_2$ -electrode potential

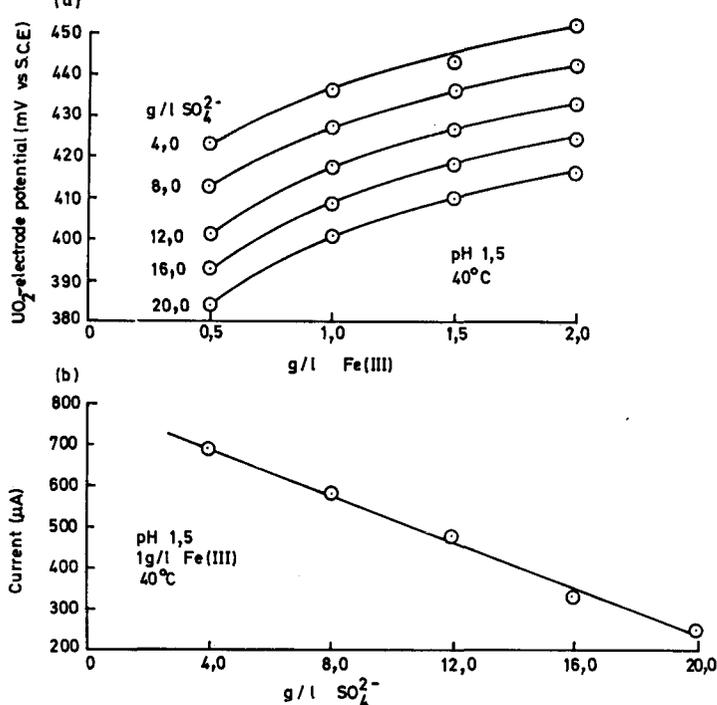


Fig. 4—Correlation between the  $UO_2$ -electrode potential, the current equivalent to the rate of leaching of  $UO_2$ , and the sulphate concentration

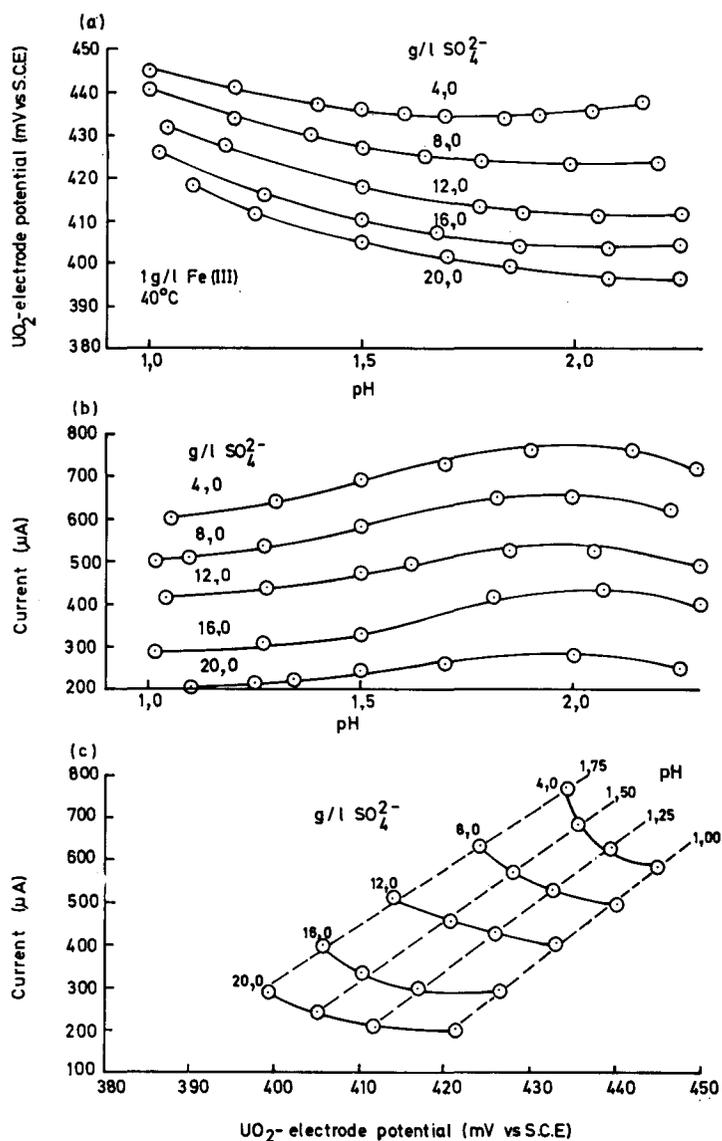


Fig. 5—Correlation between the  $UO_2$ -electrode potential, the current equivalent to the rate of leaching of  $UO_2$ , and pH

indicate a maximum in the leaching rate at a pH value of about 1,9. The net effect of variation in both pH and the sulphate concentration on the relationship between the potential and the leaching rate is shown in Fig. 5(c), from which it can be concluded that, for pH values below 2, the  $UO_2$  electrode cannot be used to predict trends in the leaching rate unless the acidity is maintained at a constant level.

A similar inverse correlation between the leaching rate and the  $UO_2$ -electrode potential with increasing phosphate concentration in solution is apparent from Fig. 6. In this case, the strong inhibition of the anodic oxidation of  $UO_2$  in the presence of phosphate<sup>2</sup> results in the observed anodic shift of the potential.

### Correlation of the Rate of Leaching with Electrode Potential

In all the work discussed above, the  $UO_2$ -electrode potential, even in the most difficult case when phosphate is present, can be correlated with the rate of leaching of a sample of pure  $UO_2$ . Significant variations in the absolute reactivity of various  $UO_2$  samples have been found<sup>2</sup>. Similar variations are to be expected among ores from different sources, and probably even within the same ore. These variations do not affect the correlation between the relative dissolution rate as indicated by the  $UO_2$ -electrode potential and the leaching power of the solution. This has been proved for the leaching of a Witwatersrand uraninite concentrate<sup>1</sup>.

However, there are two factors for which the  $UO_2$ -electrode potential can make no provision. Firstly, the dissolution, in acid, of fully oxidized uranium minerals in the ore is not an electrochemical process. Secondly, during the later stages of the leach, the extraction of uranium proceeds from the less reactive and less accessible portions of the ore particles. Therefore, the rate of recovery becomes increasingly less dependent on the solution parameters and more dependent on physical characteristics of the ore, such as the degree of liberation of uranium, the degree of hetero-

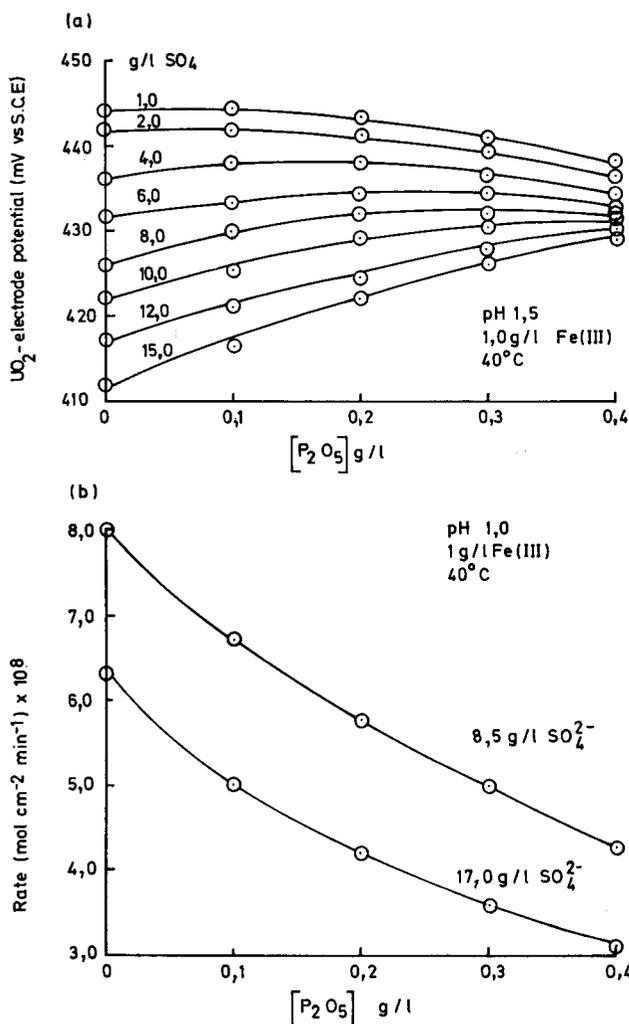


Fig. 6—Correlation between the  $UO_2$ -electrode potential, the rate of leaching of  $UO_2$ , and the phosphate concentration

- A Sampling position pachuca 2
- B Sampling position pachuca 3
- C Position of platinum electrode
- D Position of  $UO_2$  electrode

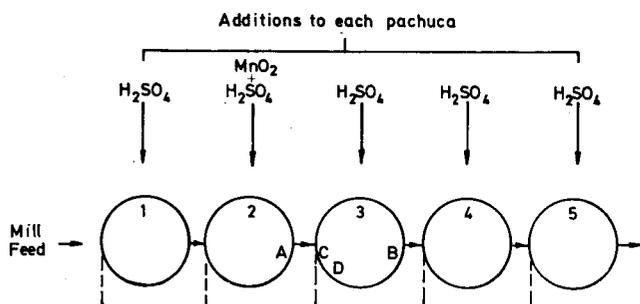


Fig. 7—A simplified plan of the leaching pilot plant and the location of the sampling points

generity, and the particle-size distribution. Obviously, the less dependent on the chemical constitution of the solution the rate of recovery becomes, the less sensitive to the true rate of recovery of uranium will be the  $UO_2$ -electrode potential. This latter point is an important reason for the lack of sensitivity of a comparison of the  $UO_2$ -electrode potential with the overall rate of recovery, i.e., when the terminal recovery is used. Therefore, it can be concluded that the measurement of the rate at which uranium can be recovered from an ore sample for a short period will be a more realistic test of the correlation with the  $UO_2$ -electrode potential than that for the overall reaction.

For this reason, a series of short-term (0,75 h) controlled leaching experiments was conducted in a typical sample of uranium ore. By *controlled experiments* is meant that pH values and the concentrations of  $SO_4^{2-}$  and Fe(III) were maintained constant throughout.

#### Variation of the Concentration of Fe(III)

As shown in Table I, the rate of recovery of uranium in the presence of varying concentrations of total iron present as Fe(III) correlates very well with the  $UO_2$ -electrode potential registered during the experiment. Except for the first and last experiments, the platinum-electrode potential was maintained around the 550 mV level by the use of  $MnO_2$  and ascorbic acid. These results emphasize the point made earlier that, because the platinum-electrode potential responds to concentrations of Fe(II) too small to affect the leaching of uranium, the  $UO_2$ -electrode potential is a much more useful aid in the control of leaching operations when the concentration of iron in solution varies.

The first experiment shows that, when enough Fe(II) is present in solution to affect the rate of leaching, both the platinum and the  $UO_2$  potentials are lower than would be expected if all the iron in solution was in the Fe(III) state. As the last two figures in Table I testify, an increase of 124 mV (i.e., from 549 to 673 mV) in the platinum electrode produces no benefit in terms of

TABLE I

RESULTS OF THE LEACHING OF AN ORE SAMPLE — THE EFFECT OF VARIATION IN [Fe(III)]

<i>Standard Conditions;</i>				
Pulp density	50% solids	Duration	0,75 h	
Temperature	25°C	Phosphate concentration	<0,03 g/l in final solution	
Controlled pH value	1,0	[Fe(II)] concentration	1,34 g/l	

[Fe(III)] g/l	[SO <sub>4</sub> <sup>2-</sup> ] g/l	Potential mV vs S.C.E.		Recovery %
		UO <sub>2</sub>	Platinum	
0,62	15,9	391	400	34,2
0,20	22,0	412	447	49,2
0,48	22,4	419	569	54,1
1,07	21,7	425	562	59,7
1,56	24,3	429	554	64,8
2,01	27,3	434	552	67,9
3,80	32,2	438	549	72,2
3,73	35,3	438	673	73,9

TABLE II

RESULTS OF THE LEACHING OF AN ORE SAMPLE — THE EFFECT OF VARIATION IN [SO<sub>4</sub><sup>2-</sup>]

<i>Standard Conditions;</i>				
Pulp density	50% solids	Duration	0,75 h	
Temperature	25°C	Phosphate concentration	<0,03 g/l in final solution	
Controlled pH value	1,5	No [Fe(II)]		

[Fe(III)] g/l	[SO <sub>4</sub> <sup>2-</sup> ] g/l	Potential mV vs S.C.E.		Recovery %
		UO <sub>2</sub>	Platinum	
1,02	10,0	424	560	58,1
1,04	20,2	418	567	55,0
0,96	27,0	412	614	53,3
0,97	41,0	406	580	51,8

TABLE III

RESULTS OF LEACHING OF AN ORE SAMPLE — THE EFFECT OF VARIATION IN pH

<i>Standard Conditions;</i>				
Pulp density	50% solids	Duration	0,75 h	
Temperature	25°C	Phosphate concentration	<0,03 g/l in final solution	

[Fe(III)] g/l	[SO <sub>4</sub> <sup>2-</sup> ] g/l	pH	Platinum mV vs S.C.E.		Recovery %
			UO <sub>2</sub>	Platinum	
1,02	21,7	1,00	425	571	59,7
1,09	22,8	1,25	421	584	57,0
1,04	20,2	1,50	418	567	55,0
1,04	21,8	1,75	414	563	52,8

TABLE IV

RESULTS OF THE LEACHING OF AN ORE SAMPLE — THE EFFECT OF VARIATION IN PHOSPHATE

<i>Standard Conditions;</i>				
Pulp density	50% solids	Duration	0,75 h	
Temperature	25°C	Phosphate concentration	<0,03 g/l in final solution	
Controlled pH value	1,0			

[Fe(III)] g/l	[SO <sub>4</sub> <sup>2-</sup> ] g/l	[P <sub>2</sub> O <sub>5</sub> ] g/l	Potential mV vs S.C.E.		Recovery %
			UO <sub>2</sub>	Platinum	
2,70	49,0	0,072	425	563	60,8
2,64	45,4	0,430	437	576	55,1
2,71	48,0	2,120	456	574	45,6
2,55	46,2	3,720	443	580	37,2

the rate of recovery of uranium. As expected from the solution conditions, the UO<sub>2</sub>-electrode potential was the same for both experiments.

*Variation of the Sulphate Concentration, pH, and Phosphate Concentration*

The data given in Table II confirm the expected trend, that an increase in the SO<sub>4</sub><sup>2-</sup> concentration in the leaching solution at concentrations of commercial interest decreases both the UO<sub>2</sub>-electrode potential and the rate of recovery of uranium.

Although it was demonstrated that the rate of leaching of pure UO<sub>2</sub> increases with a pH value of up to 1,9, the data in Table III show that the reverse is the case for the ore sample. This must result from the fact that the optimum pH value for the leaching of the predominant constituents of the ore is lower than that for pure UO<sub>2</sub>. There was a positive correlation between the UO<sub>2</sub>-electrode potential and the rate of recovery at all the pH values tested, a result that could not be predicted from a study of the leaching of pure UO<sub>2</sub>.

It was fortunate that the sample of ore used in the experiments yielded very little phosphate (below 0,03 g/l).

Table IV gives results from the experiments in which phosphate was added to the leaching solution. It can be seen that the rate of recovery decreases steadily with increasing phosphate additions, whereas the UO<sub>2</sub>-electrode potential passes through a maximum. Only the first two results in Table IV are relevant to practice because the conditions at the maximum and on the far side of these results reflect extremely high concentrations of P<sub>2</sub>O<sub>5</sub>, which are intolerable to uranium-leaching operations.

It is clear that the effect of phosphate may not be easily recognizable in practice and that, for the UO<sub>2</sub> electrode to give reliable correlation with leaching rate, steps must be taken to control the level of phosphate in solution.

### Pilot-plant Tests

Tests were conducted on a uranium-leaching pilot plant.

A simplified diagram of the leaching plant, the additions made to each of the five pachucas, and the

approximate position of the  $UO_2$  electrode are given in Fig. 7. The rate of addition of  $MnO_2$  was adjusted so that the redox potential registered by the platinum electrode in pachuca 3 would be maintained at a preset value. This adjustment was done usually by automatic feed-back control. The  $UO_2$  reference electrode probe was installed on the 13th of January, 1972, and its potential was monitored for a period of six weeks, during which the leaching plant was operated continuously. During the major portion of the test, only the regular values for shift-composite recovery were available for comparison with the  $UO_2$ -electrode potentials. As these values were calculated from chemical analyses of composite samples that

comprised eight-hourly samples from the outlet of pachuca 5, they obviously were far too insensitive to short-term changes in pachuca 3. To improve definition of the relationship between the  $UO_2$ -electrode potential and the rate of recovery of uranium, a series of sampling trials was conducted over a period of five days, during which the amount of uranium leached in pachuca 3 was obtained as the difference between the uranium content of samples taken from the outlet of pachuca 2 and the outlet of pachuca 3.

*Data on Samples Collected on 21st February, 1972*

During this period the plant was run under steady-state conditions (i.e., the  $UO_2$ -electrode potential and

the acidity were kept as constant as possible), and checks were made on whether reproducible rates of recovery were obtained over a number of hours. The data are given in Table V.

The  $MnO_2$  feed was maintained manually during this period. The platinum-electrode potential decreased as a result of an error in manual control but, because the original setting was too high, this made no difference to the leaching rate. Very significant is the fact that both the  $UO_2$ -electrode potential and the rate of recovery of uranium from pachuca 3 are approximately constant over this period.

*Data on Samples Collected on 24th February, 1972*

During this period, the  $MnO_2$  feed was automatically controlled against a redox potential of 610 mV. The aim of the experiment was to check the effect of the variation of pH on the rate of recovery and the  $UO_2$ -electrode potential. Accordingly, the pH value of the solution in pachuca 3 was increased from 1,5 to 2,4, and then decreased to 1,8. The results are shown in Fig. 8.

During this time, the  $UO_2$ -electrode potential decreased from 498 to 448 mV, and then rose to approximately 493 mV. Originally, this variation was ascribed purely to pH changes. However, a subsequent examination of the analyses for Fe(III) shows that, because of low acid levels, the total iron in solution had decreased to 0,4 g/l. (The concentration of Fe(II) is assumed to be low because of the high platinum potential.) In all probability, the actual figure was lower because of the tendency of plant operators to overshoot the endpoint in their volumetric determination of Fe(III).

Reference to Fig. 8 shows that the trend set by the rate of recovery of uranium is followed closely by the  $UO_2$ -electrode potential. This is a most important demonstration that the  $UO_2$  electrode gives a direct indication of the leaching power of the solution. On the other hand, the variation in recovery is not reflected at all by any change in the redox potential. Admittedly, the platinum-electrode potential ensures that enough  $MnO_2$  is added

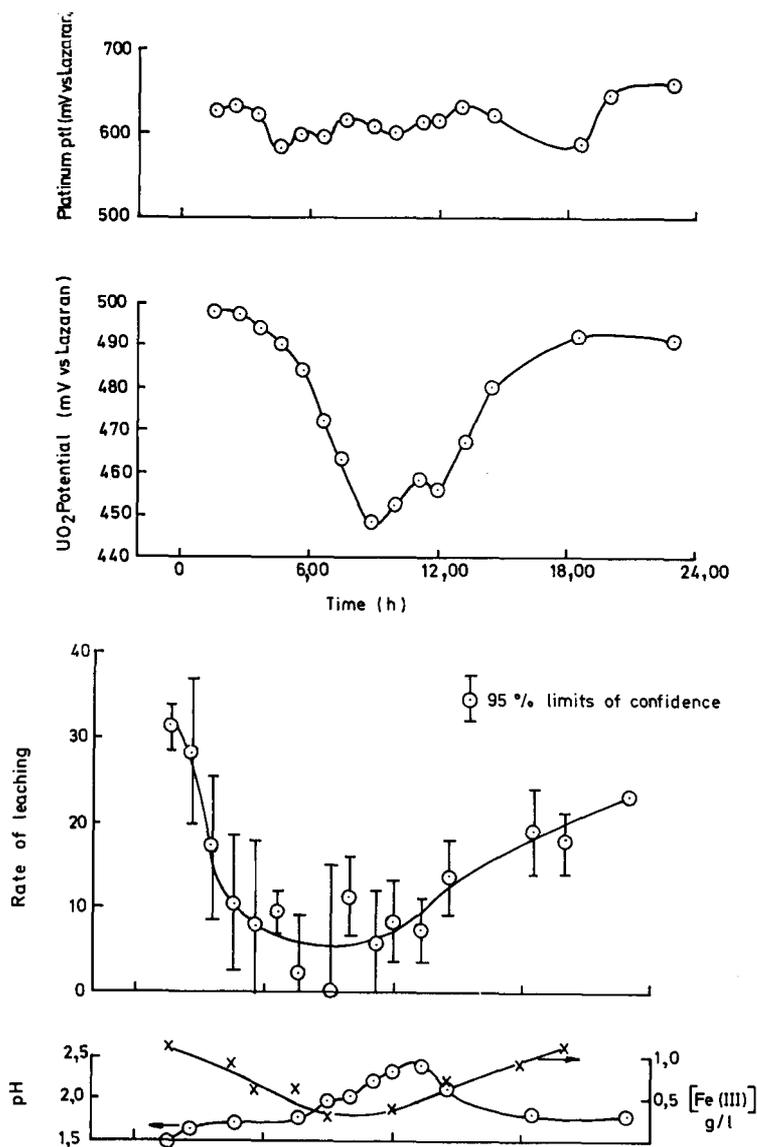


Fig. 8—Data obtained from samples collected at the pilot plant on 24 February, 1972

TABLE V  
RESULTS OF THE SAMPLING OF PACHUCAS 2 AND 3 ON THE PILOT-PLANT. DATE: 21st FEBRUARY, 1972

Pachuca	Time	pH value	Fe(III) g/l	Potential mV vs Lazaran		Average analysis for U <sub>3</sub> O <sub>8</sub> p.p.m.	Rate of leaching Arbitrary units
				UO <sub>2</sub>	Platinum		
2	12h10	1,7	1,0	480	631	51,0	19,5
3						31,5	
2	1h20	1,65	—	482	627	63,5	22,0
3						41,5	
2	2h00	1,8	1,1	482	609	69,0	25,0
3						54,0	
2	2h55	1,65	—	481	585	72,0	21,5
3						45,5	
2	3h50	1,8	1,2	480	560	72,0	26,5
3						45,5	
2	4h45	1,65	—	480	570	72,5	20,5
3						52,0	
2	5h50	1,65	1,2	480	605	66,0	19,5
3						46,5	
2	6h15	1,65	—	481	597	81,0	22,5
3						58,5	

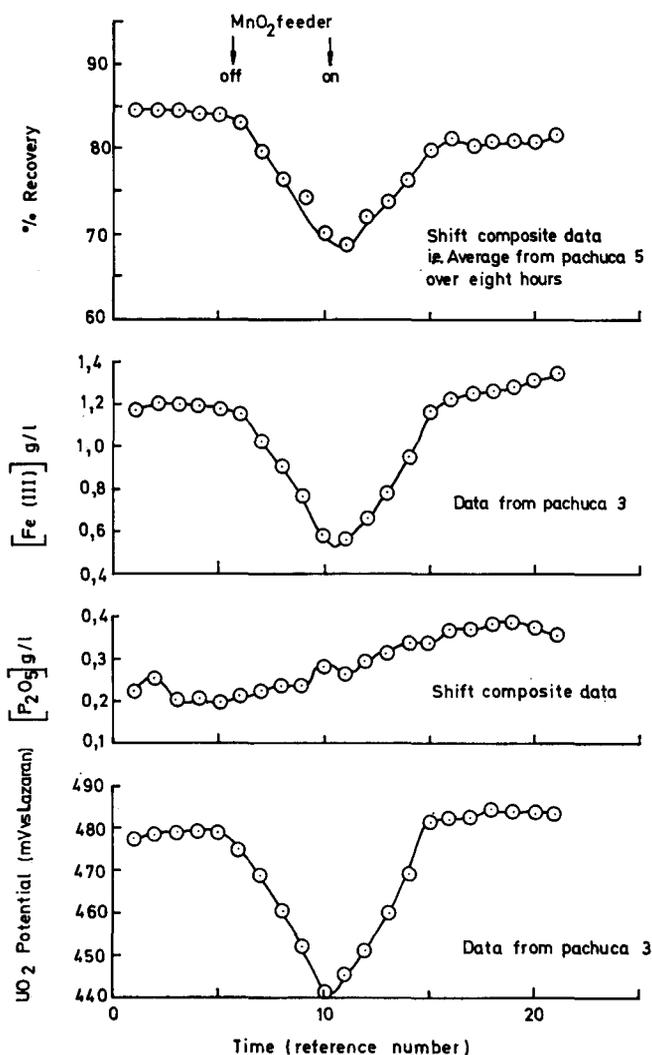


Fig. 9—Summary of pertinent pooled data from the pilot plant for the period 13th to 22nd January, 1972

to keep all the iron in the Fe(III) state, but the UO<sub>2</sub>-electrode potential indicates immediately if there is enough Fe(III) present to ensure that economic recovery of uranium is maintained.

#### Long-term Trends

The UO<sub>2</sub> electrode operated continuously for six weeks before it failed, and during that period a continuous record of its potential was obtained. It was felt that a long-term assessment of the plant's figures, coupled with information supplied by the UO<sub>2</sub>-electrode potential, would be of value.

In order that short-term trends due to minor fluctuations in operating conditions might be minimized and scatter in the shift-composite analyses reduced, a moving average over five shifts was calculated. Two periods of operation were considered, namely 13th to 22nd January, 1972, and 29th January to 20th February, 1972, and the essential results are plotted in Figs. 9 and 10.

During the first period (Fig. 9), the MnO<sub>2</sub> feeder was out of operation for 36 hours, and the ratio of Fe(III) to Fe(II) in solution decreased as a direct result. This was accompanied by a general decrease in the overall recovery of uranium and, as expected, a decrease in both the UO<sub>2</sub>- and platinum-electrode potentials.

In the second period (Fig. 10), an overall increase in the UO<sub>2</sub>-electrode potential, but not in the overall recovery figures, was noted. However, probably owing to the recycling of a proportion of the

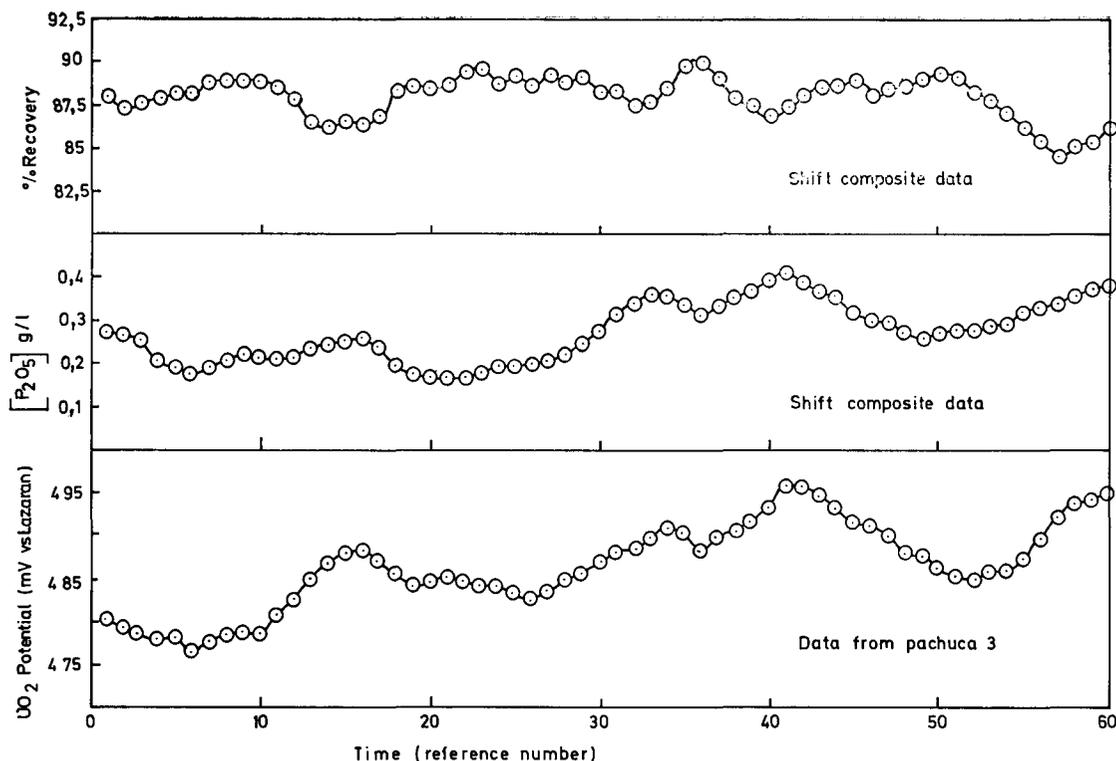


Fig. 10—Summary of pertinent pooled data from the pilot plant for the period 29th January to 20th February, 1972

leach liquor, the average phosphate levels in solution gradually increased. Careful reference to Fig. 10 indicates that the  $\text{UO}_2$ -electrode potential correlates with the phosphate concentration in solution, both of which are inversely related to the recovery figures. As already emphasized, this reflects a serious limitation in the use of the  $\text{UO}_2$  electrode as a control device. Although there is a correlation, the fact that it is negative makes it hard to recognize, and the electrode may not be suitable for a plant in which phosphate levels vary considerably.

#### THE INDUSTRIAL POTENTIALITIES OF THE $\text{UO}_2$ ELECTRODE

Originally, it was envisaged that the  $\text{UO}_2$  electrode would be used on a plant as a control device. However, as the rate of recovery of uranium in the presence of phosphate does not correlate positively with the  $\text{UO}_2$ -electrode potential, the electrode would not be an ideal control device on plants processing uranium ores that contain apatite (or other acid-soluble phosphatic minerals). It should be noted that the platinum-electrode potential

would similarly give no warning that the rate of leaching had decreased owing to the presence of excessive amounts of phosphate. Nevertheless, the rate of recovery of uranium does correlate positively with the effect on the  $\text{UO}_2$ -electrode potential of varying concentrations of  $\text{Fe(III)}$ ,  $\text{H}^+$ , and  $\text{SO}_4^{2-}$ , and so the electrode does possess control potentialities on plants not troubled by high levels of phosphate in solution.

In addition, the electrode might still be used universally as a warning device or a diagnostic tool. From the foregoing it is apparent that, at a constant platinum potential, the two most economically significant factors that contribute to an increase or decrease in the  $\text{UO}_2$ -electrode potential are the concentrations of  $\text{Fe(III)}$  and of phosphate. If the  $\text{UO}_2$ -electrode potential is seen to vary, a simple routine determination of the  $\text{Fe(III)}$  in solution at constant platinum potential and acidity will serve to indicate which is causing the effect. The necessary steps might be taken to prevent a decrease in the uranium extraction. Normally this would be evident only long after the event, when shift samples were analysed.

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