



CANADA

**SURFACE AREA DETERMINATION
OF MAGNESIUM POWDER WITH
CHROMIUM-51 TRACER SOLUTIONS**

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by

H. P. DIBBS

MINERAL SCIENCES DIVISION

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SURFACE AREA DETERMINATION OF MAGNESIUM POWDER
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H.P. Dibbs^{*}

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SYNOPSIS

A study has been made of the adsorption of chromium-51, from aqueous solutions of labelled potassium dichromate, on to coarse magnesium powder at room temperature. This has led to a simple method for the determination of the surface area of the powder.

^{*} Scientific Officer, Mineral Sciences Division, Mines Branch,
Department of Mines and Technical Surveys, Ottawa, Canada.

Direction des Mines

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DETERMINATION DES SURFACES DE POUVRE DE
MAGNESIUM PAR DES SOLUTIONS DE CHROME RADIOACTIF

par

H.P. Dibbs^A

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RÉSUMÉ

On a fait des expériences tendant à
déterminer le degré d'absorption du chrome-51,
tiré de solutions aqueuses de bichromate de potassium
marqué, par la poudre de magnésium grossière, à
la température de la pièce. On en a tiré un procédé
simple de détermination de l'étendue superficielle
de cette poudre qui participe à la réaction.

^A Chargé de recherches, Division des sciences minérales,
Direction des Mines, Ministère des Mines et des Relevés
techniques, Ottawa, Canada.

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INTRODUCTION

Several methods are available for the determination of the surface area of fine-grained particles. These range in complexity from the B.E.T. gas adsorption technique (1) to a straightforward long-chain fatty acid adsorption determination (2). In many instances of routine practical application, it is sufficient to have a relative determination of surface area between different batches of material, and several satisfactory methods are available. However, when the surface area to be measured is small, say, of the order of $100 \text{ cm}^2/\text{g}$, difficulties arise due to the fact that for most of the methods the lower limit of determination is set by the analytical technique which is used to measure the variable related to surface area. The use of radioisotopes can extend this lower limit considerably, due to the greatly enhanced measuring efficiency which they offer. In the case of a surface adsorption method this limit is set only by the maximum specific activity of the element adsorbed and the radiation-detection efficiency of the counting system.

An example of the scope of this technique has been given by Lewis and Plumb (3) in an examination of the behaviour of aluminum towards stripping solutions. In this work, it was possible to study the film formed on small areas of aluminum after immersion in a chromic/phosphoric acid solution in which both the chromium and the phosphorus were labelled. Somewhat

similar studies on the nature of the passive layer formed on iron (4) and other metals (5) have also been performed. Chromates and dichromates have been used for a number of years to enhance the corrosion resistance of certain metals, although the exact mechanism of the process is still in doubt. It is known that magnesium may be at least partly protected by immersion in an aqueous solution of potassium dichromate (6, 7). With this in mind an investigation was undertaken into the build-up of a chromium-containing layer on magnesium in an aqueous potassium dichromate solution in which the chromium was labelled with chromium-51. In this manner it was considered possible that a relationship between surface area and activity adsorbed could be obtained.

EXPERIMENTAL DETAILS

The magnesium powder used in this work was of high purity (99.9%) and in the form of irregularly shaped particles. No pretreatment of the powder was undertaken and all the experiments were performed at room temperature. The measurement of the build-up of chromium on the surface of the magnesium was made by agitating a weighed amount of the powder with 15 ml of an aqueous solution of chromium-51 labelled potassium dichromate. This was performed in the reaction vessel illustrated in Figure 1. After a given time interval, usually one hour, the shaking was stopped and the bulk of the active solution decanted from the reaction vessel. The remainder of the active solution was removed by washing with

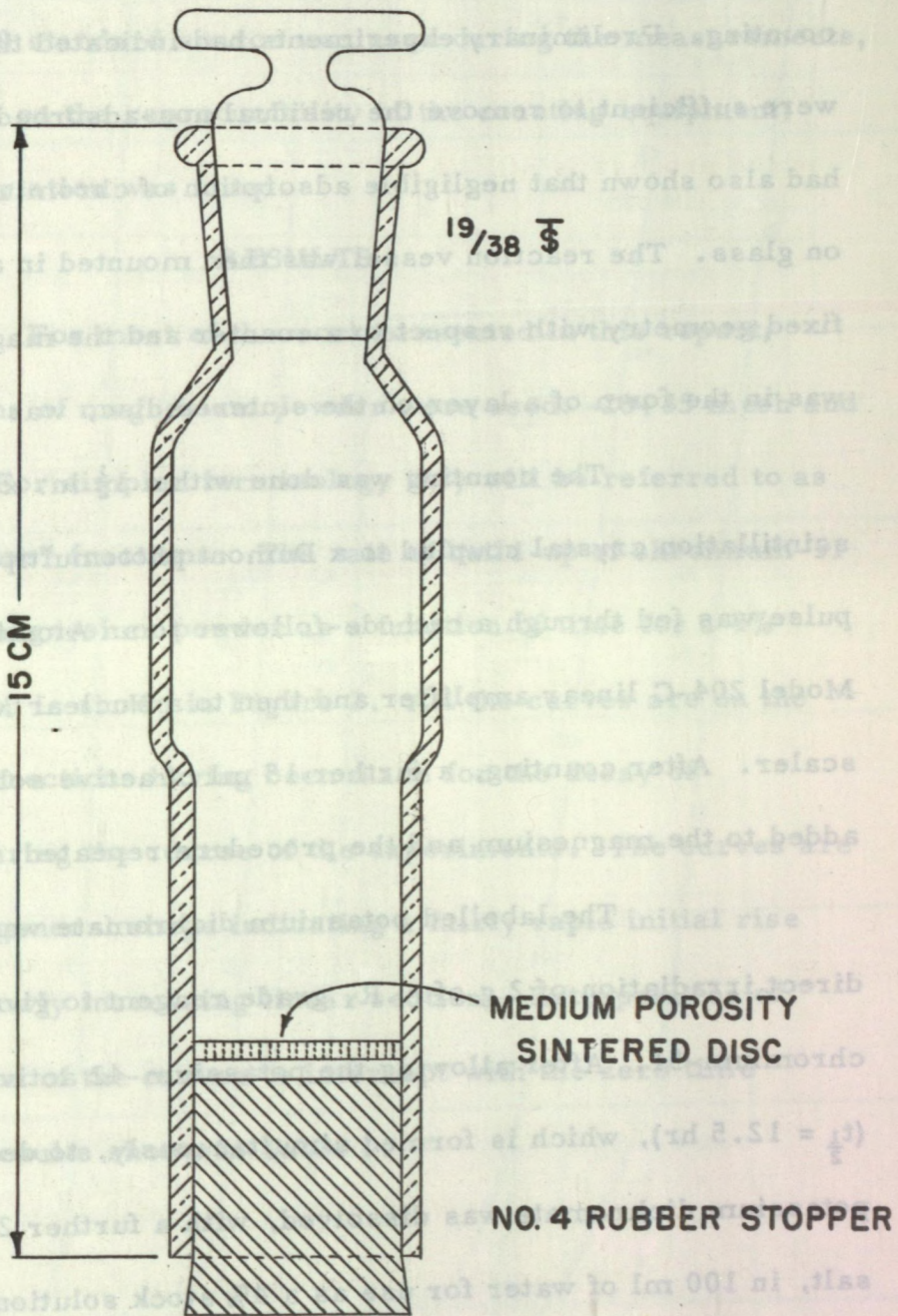


FIG. 1- REACTION VESSEL

distilled water. A filter pump was used to remove the final traces of water and also served to give a uniform layer of magnesium for counting. Preliminary experiments had indicated that three washings were sufficient to remove the residual non-adsorbed activity and had also shown that negligible adsorption of chromium-51 occurred on glass. The reaction vessel was then mounted in a position of fixed geometry with respect to a counter and the magnesium, which was in the form of a layer on the sintered disc, was counted.

The counting was done with a $1\frac{1}{2}$ in. x $1\frac{1}{2}$ in. scintillation crystal coupled to a Dumont photomultiplier tube. The pulse was fed through a cathode-follower to an Atomic Instrument Model 204-C linear amplifier and then to a Nuclear Model 165 scaler. After counting, a further 15 ml of active solution was added to the magnesium and the procedure repeated.

The labelled potassium dichromate was obtained by direct irradiation of 2 g of A.R. grade reagent to give 70 mc of chromium-51. After allowing the potassium-42 activity ($t_{\frac{1}{2}} = 12.5$ hr), which is formed simultaneously, to decay, the potassium dichromate was dissolved, with a further 2 g of inactive salt, in 100 ml of water for use as a 4% stock solution. Suitable aliquots of this stock solution were then added to 4% and 10% solutions of inactive potassium dichromate to give a chromium-51 specific activity in the range of 5-10 μ c/ml. As chromium-51

has a relatively short half-life of 27.8 days, an aliquot of the active solution used for each experiment was counted before every run. A cobalt-60 standard source was used during the measurements, to act as a check on the reproducibility of the counting equipment; no significant variation was found.

RESULTS

For most of the work presented in this report, two size fractions of magnesium powder were used: -28+35 mesh and -35+65 mesh. For simpler terminology they will be referred to as "coarse" and "fine" fractions. The rate of build-up of chromium-51 activity on the magnesium powder as a function of time for a 4% $K_2Cr_2O_7$ solution is shown in Figure 2. All the curves are on the same scale, corrections having been made for the decay of chromium-51 during the course of the experiments. The curves are all of the same general shape indicating a fairly rapid initial rise followed by a slowly increasing linear section. Extrapolation of the linear section of the curves to intercept with the zero time axis gives the results shown in Table 1.

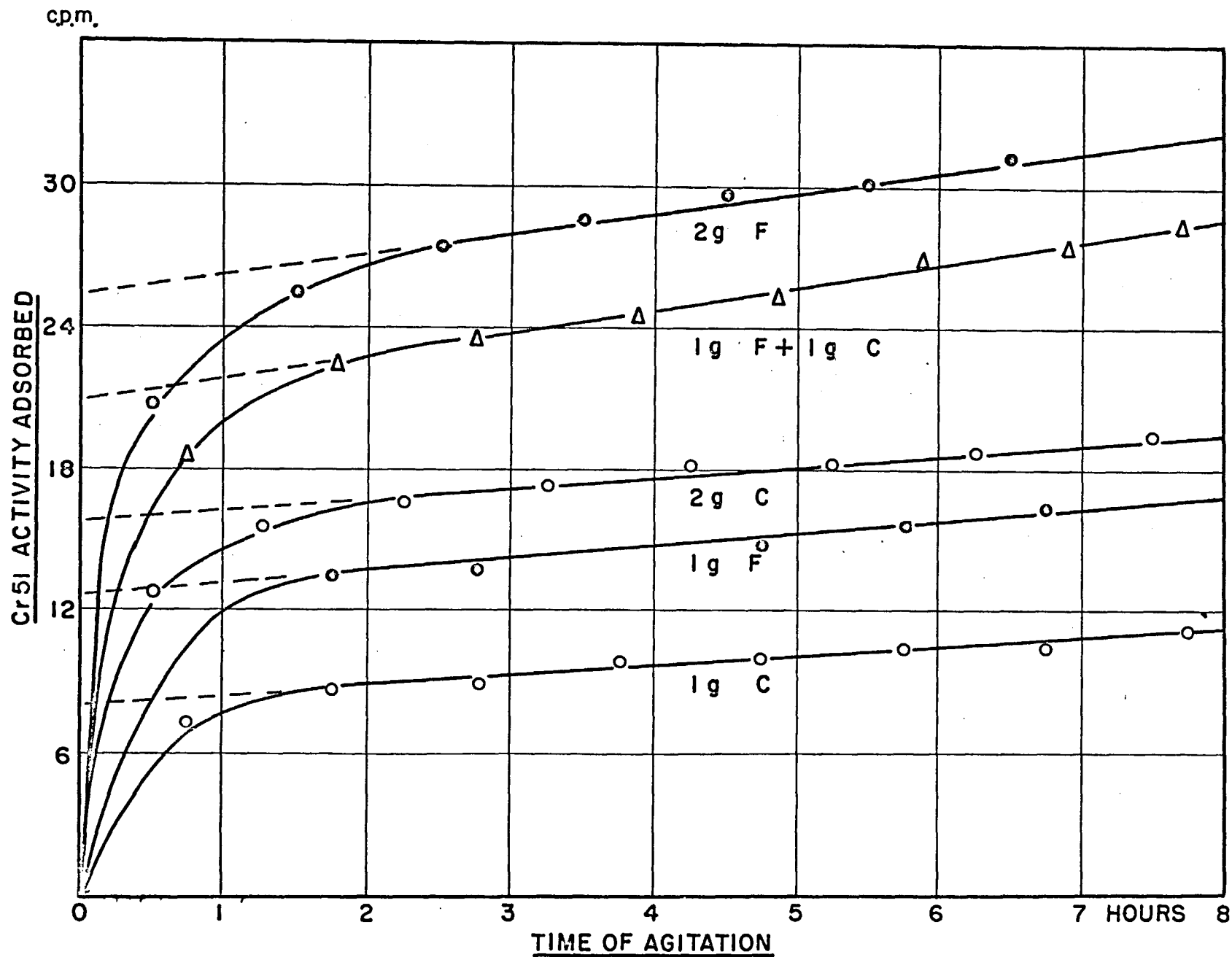


FIG.2 - ADSORPTION OF Cr51 ON MAGNESIUM FROM 4% $K_2Cr_2O_7$ SOLUTION.
(C- COARSE SIZE FRACTION, F- FINE SIZE FRACTION)

TABLE 1

Adsorption Curve Intercepts for 4% $K_2Cr_2O_7$ Solution

Coarse		Fine	
Weight	Intercept	Weight	Intercept
1 g	7.9 c.p.m.	1 g	12.8 c.p.m.
2 g	15.9 c.p.m.	2 g	25.4 c.p.m.
1 g Coarse + 1 g Fine; Int. = 20.65 c.p.m. (experimental) 20.7 c.p.m. (calculated)			

It will be seen from the above table that the intercepts for the 1 g and 2 g samples of the same grade stand in a close 1:2 ratio with each other, and also that a mixture of 1 g coarse and 1 g fine gives a linear addition of the two grades separately. This serves to show that the phenomenon studied is of a regular nature.

A similar set of results was obtained on the same size fractions of magnesium using a 10% solution of potassium dichromate, as shown in Figure 3. They have been corrected to the same activity scale in terms of c.p.m./ml of dichromate solution as those in Figure 2, so that the two sets of curves are comparable. The intercepts, as above, are given in Table 2. As in Table 1, good agreement between different weights is obtained.

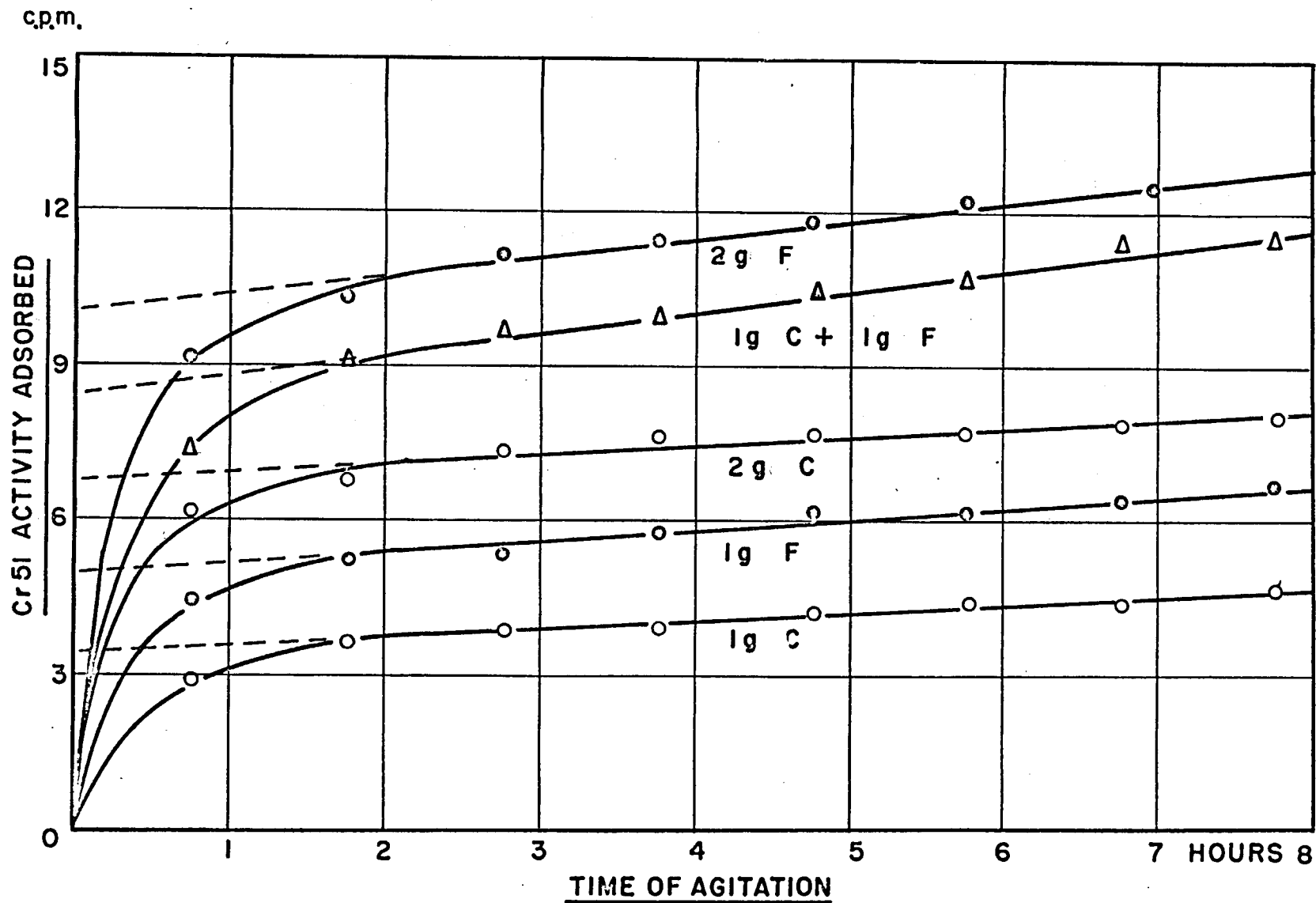


FIG. 3-ADSORPTION OF Cr51 ON MAGNESIUM FROM 10% $K_2Cr_2O_7$ SOLUTION.
 (C-COARSE SIZE FRACTION, F- FINE SIZE FRACTION)

TABLE 2

Adsorption Curve Intercepts for 10% $K_2Cr_2O_7$ Solution

Coarse		Fine	
Weight	Intercept	Weight	Intercept
1 g	3.36 c.p.m.	1 g	4.95 c.p.m.
2 g	6.76 c.p.m.	2 g	10.0 c.p.m.
1 g Coarse + 1 g Fine; Int. = 8.4 c.p.m. (experimental) 8.3 c.p.m. (calculated)			

From the data in Tables 1 and 2, we can obtain the ratio of the amounts of chromium-51 adsorbed, in terms of the intercept ratios, between 1 g and 2 g samples of both size fractions for the two different solution concentrations. This is shown in Table 3.

TABLE 3

Adsorption Intercept Ratios

Fraction ratio	Soln. conc.	
	4%	10%
$\frac{1 \text{ g Fine}}{1 \text{ g Coarse}}$	1.62	1.47
$\frac{2 \text{ g Fine}}{2 \text{ g Coarse}}$	1.59	1.48

These results show remarkably close agreement between 1 g and 2 g samples for each solution, and also good agreement between the two solution concentrations. If it is assumed that the amount of chromium-51 adsorbed per unit area is independent of particle size, this gives a measure of the relative surface area of the two fractions.

In an attempt to determine the absolute surface area of the magnesium powder, a number of samples of high-purity magnesium metal of known geometrical area (between 1-2.5 cm²/sample) were mounted in Lucite and carefully polished. The rate of build-up of activity from the high specific activity (4%) stock solution was then measured. Similar curves to those in Figures 2 and 3 were found. Autoradiographs of the samples, however, indicated that some penetration of the active solution had occurred at the magnesium/Lucite interface. In an effort to overcome this, the interfacial section around the magnesium was carefully milled out and the sample again counted. Fresh autoradiographs were then taken and the procedure repeated until little evidence of penetration remained. By correlating the activity adsorbed on the mounted samples with their known geometrical surface area, it was calculated that for the three samples examined (assuming the geometrical and real surface area to be equivalent) one square centimetre of surface was equivalent to 2.8×10^{-2} c.p.m. in terms of the magnesium powder. Thus, for example, 1 gram of the coarse size fraction in 4% solution with an intercept of 7.9 c.p.m. (Table 1) would correspond to a surface

area of about $280 \text{ cm}^2/\text{g}$. This result should be regarded primarily as a guide, since the counting rates of the samples towards the end of the milling sequence were low and of the same order as the natural background. However, this figure was confirmed as being approximately correct, by the use of a different technique involving the adsorption of carbon-14 labelled oleic acid from a toluene solution on to a known weight of magnesium (8). By measuring the amount of oleic acid present in solution before and after adsorption, the amount which has been adsorbed on the surface may be found. As this forms a monolayer in which the area of the oleic acid molecule is known (9), an assessment may be made of the total surface area of the powder. This procedure gave an area of $360 \text{ cm}^2/\text{g}$ for the coarse size fraction.

DISCUSSION

The inhibitive action of oxidized chromium anions in limiting corrosive attack is well known and is usually attributed either to the production of a tightly adsorbed film (10) or to the formation of a protective (precipitation) film on the metal surface (11). For the $\text{Mg}/\text{K}_2\text{Cr}_2\text{O}_7$ system, since the specific activity of the chromium-51 is known, the weight of chromium which has been incorporated into the magnesium surface may be calculated. This is given below (Table 4) for both the 4% and 10% solutions from the intercept points. It will be noted that the weight of chromium is effectively independent of solution concentration. Assuming a

TABLE 4

Weight of Chromium Adsorbed at Intercept Points

4% solution		10% solution	
Weight	Cr adsorbed	Weight	Cr adsorbed
<u>Coarse</u>		<u>Coarse</u>	
1 g	300 μg	1 g	318 μg
2 g	600 μg	2 g	640 μg
<u>Fine</u>		<u>Fine</u>	
1 g	485 μg	1 g	470 μg
2 g	978 μg	2 g	950 μg

surface area of approximately $300 \text{ cm}^2/\text{g}$ for the coarse size fraction, this corresponds to approximately $1.0 \mu\text{g Cr}/\text{cm}^2$ adsorbed on the surface. Although only a small amount of information is available concerning the structure of dichromate ion, it is apparent from its relatively large overall size (12) that, if the chromium were present on the surface as MgCr_2O_7 , a surface layer of many atomic thicknesses would be found. It is improbable that this multilayer would be stable to washing, because of the high solubility of the salt (13). Similarly, multilayer adsorption of the dichromate ion itself would not likely be stable, since all except a monolayer should be washed off. However, as may be seen from Figures 2 and 3, the chromium layer is stable and continues to increase with time.

The increased resistance of magnesium, which has been treated with dichromate, to attack by water is shown in Figure 4. When untreated magnesium is placed in water and the change in pH of the water with time is measured, curve A results, which rapidly approaches the limiting value of 10.3. With the treated magnesium, however, only a slight increase in pH occurs over a comparable time, as shown by curve B.

Magnesium is normally covered with an oxide or hydrated oxide layer. Since the molecular volume of the oxide is less than that of the metal, the resulting oxide layer will tend to be discontinuous or cellular (14), leaving points of attack available on the surface. It is likely, therefore, that the passivating action of the dichromate will tend to reinforce the oxide film at these points, associated with a concomitant precipitation of insoluble chromium oxide which will be incorporated in the film. As the film thickness increases, the resultant growth will continue either by further diffusion of dichromate through discontinuities in the oxide film or by diffusion of magnesium ions through the film itself. This mechanism would account for the relatively rapid initial increase in activity followed by the much slower linear section of the curve.

Thus, assuming that the thickness of the passivating layer formed on the magnesium surface is independent of the state of subdivision of the metal, a simple method, requiring only a limited amount of equipment, is available to measure both the

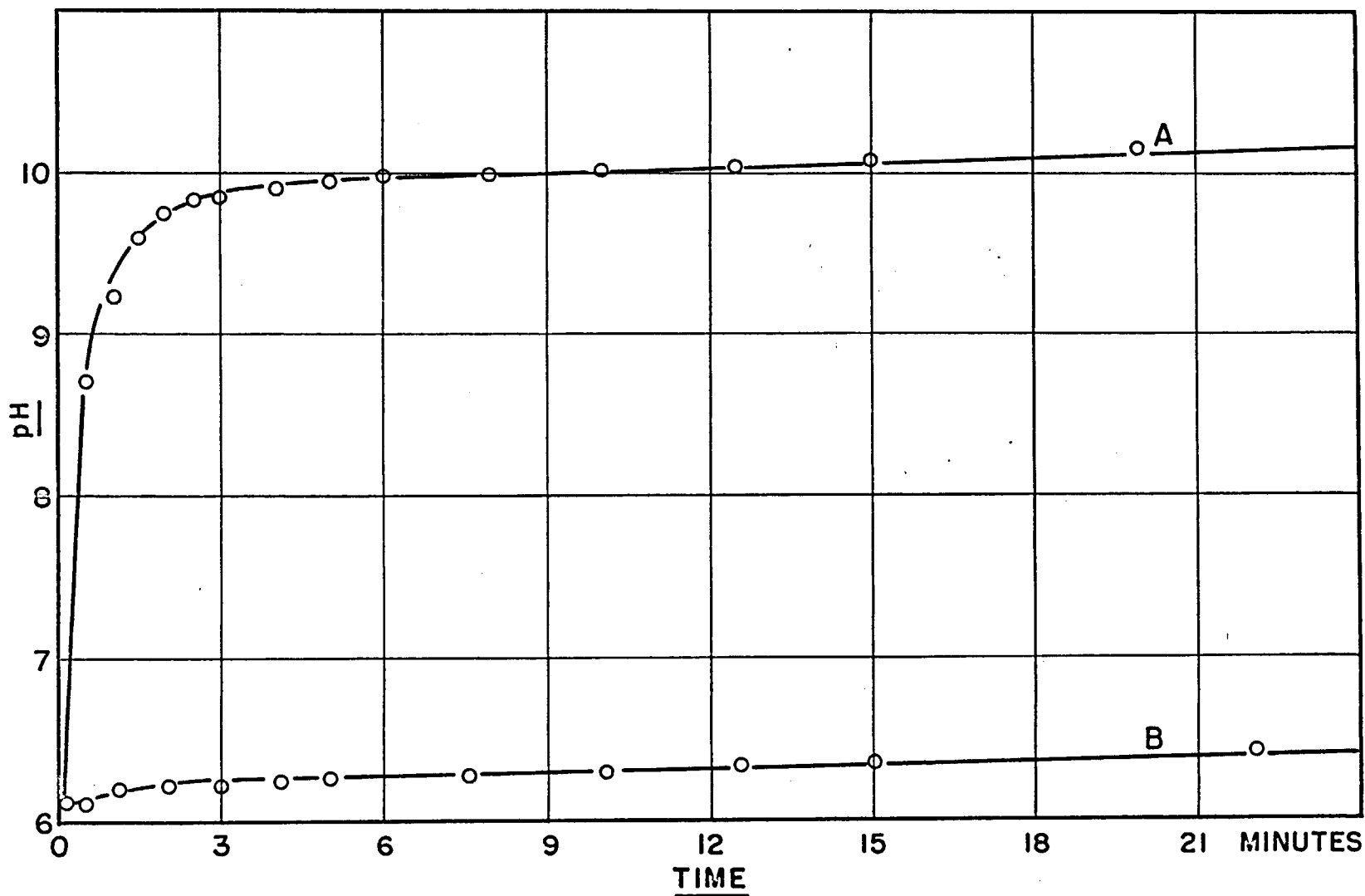


FIG. 4 - CHANGE OF pH OF WATER IN THE PRESENCE OF MAGNESIUM.
 (A-UNTREATED SAMPLE, B-TREATED SAMPLE)

absolute and relative surface areas of coarse magnesium powder in a range which is not easily determined by conventional techniques.

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HPD:DV

