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**SOME EXPERIMENTAL RESULTS ON THE
SORPTION OF Cs BY SUBMICRON
W-10% Ta AND Ta POWDERS**

by

G.F. DE BENI, O. GAUTSCH and G. HODAPP

1971



**Joint Nuclear Research Centre
Ispra Establishment-Italy**

**Materials Division
Physical Chemistry Section**

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Luxembourg, December 1971 — 24 Pages — 19 Figures — BF 40.-

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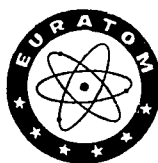
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ABSTRACT

Submicron W-10% Ta and Ta powders were loaded with Cs at powder temperatures between 600 and 800°C, and Cs-vapour pressures ranging from about 0.01 to 20 mm Hg (sorption-desorption cycles). The Cs saturation loadings were determined by a Cs¹³⁴-tracer-method and the corresponding equilibrium pressures of the Cs-vapour were obtained from the temperature of a liquid Cs-reservoir. The "pressure-temperature-loading" characteristics of the Cs-Ta system showed that the saturation loadings are, at given Cs-pressures, proportional to the oxygen content of the powders, i.e., to the amount of Ta₂O₅. This oxide probably reacts with Cs to form compounds of the type Ta₂Cs_xO₅, with $x = 2, 4, 6$.

KEYWORDS

POWDERS
TUNGSTEN BASE ALLOY
TANTALUM ALLOYS
TANTALUM
CESIUM
TEMPERATURE
VAPOR PRESSURE
DESORPTION
CESIUM 134
TRACER TECHNIQUES
RADIOISOTOPES
EQUILIBRIUM
TANTALUM OXIDES
ISOTHERMAL PROCESSES
DIAGRAMS
HYSTERESIS

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S u m m a r y

Submicron W-10%Ta and Ta powders were loaded with Cs at powder temperatures between 600°C and 800°C, and Cs-vapour pressures ranging from about 0.01 to 20 mm Hg (sorption-desorption cycles). The Cs saturation loadings were determined by a Cs¹³⁴ - tracer-method and the corresponding equilibrium pressures of the Cs-vapour were obtained from the temperature of a liquid Cs-reservoir. The "pressure-temperature-loading" characteristics of the Cs-Ta system, showed that the saturation loadings **are**, at given Cs-pressures, proportional to the oxygen content of the powders, i.e., to the amount of Ta₂O₅. This oxide probably reacts with Cs to form compounds of the type Ta₂Cs_xO₅, with x = 2, 4, 6.

The loading isothermes (obtained by plotting the logarithm of the Cs-pressure p vs the saturation loading L at constant powder temperature T) are composed of more or less pronounced plateaus, and vertical parts. A strong hysteresis effect was observed on desorption. The isosteres (log p vs 1/T at constant L) of the desorption branches of the isotherms have steeper slopes than those of the sorption branches. It is supposed therefore that the hysteresis is due to a difference in the energy of activation for the formation and decomposition of a given compound.

On the plateaus, which are situated in the Cs-pressure range of 1-10 mmHg, the loadings vary between 10-50 mgCs/g for a pressure change of 1 mm Hg, and the pressure variations are 0-0.3 mmHg/°C. A Cs-reservoir of the Ta-Cs type, used in thermionic converters to maintain a given Cs-pressure and to compensate for possible Cs-losses, should, in principle, operate on the plateaus of the desorption branches of the isotherms, in order to avoid hysteresis.

1. Introduction *)

The scope of this work was to measure the saturation amounts of Cs which could be sorbed by submicron W-10%Ta and Ta powders at powder temperatures of 600-800°C and Cs-vapour pressures between 0.01 and 20 mm Hg. Such Cs-loaded powders could possibly be used as Cs-reservoirs in thermoionic converters (1), in order to maintain at given operating temperatures a self-regulating Cs-pressure in the range of 1-10 mm Hg, and to assure optimum converter operation without external control. The reservoirs must also be able to supply to the converter volume sufficient amounts of Cs to compensate for Cs-losses which might occur; e.g., as a result of reaction of Cs with internal surfaces of the converter.

Earlier experiments (1) with a W-10%Ta powder of a specific surface of $0.023 \text{ m}^2/\text{g}$ showed that unexpectedly high quantities of Cs, corresponding to about 100 monolayers, were sorbed at 800°C and Cs-pressures of 0.01-10 mm Hg. It was suggested (1) that such high Cs-loadings were not the result of a physical adsorption but, possibly, of a chemical reaction between the Ta, Cs and O_2 .

Since the possible formation of such Cs-compounds would be of interest to converter application (in analogy to Cs-graphite compounds), three submicron powders of high specific surface were selected as samples for the present experiments, i.e., a W-10%Ta powder with an elevated O_2 -concentration and two Ta-powders with different O_2 -contents.

The sorption apparatus and the experimental procedure were the same as those already described in detail previously (2), based on tracer technique, using Cs^{134} . Some experimental data are shown in table 1. Before the experiment the powders were outgassed at 850°C with the rest of the apparatus at 450-650°C until a vacuum of better than $1 \cdot 10^{-6}$ was reached, which improved at room temperature to

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better than $3 \cdot 10^{-8}$ mm Hg. The leak rates of the apparatus were before and after sealing below $3 \cdot 10^{-9}$ Torr-liter/sec.

The measurements were always started with a powder temperature of 800°C and with low Cs-pressures. The temperature of the liquid Cs-pool was varied in steps between 150 and 420°C (the rest of the sorption apparatus was kept above 450°C) and the corresponding Cs-pressures were obtained by a p-T relation reported in reference (3). At a given initial Cs-pressure the Cs¹³⁴-activity on the sample (which is related to the Cs-loading by means of the specific activity) was recorded as a function of time. When the Cs-loading had reached a saturation value (generally within 4 hours), the Cs-temperature was increased to the next desired value and the saturation loading determined, together with the corresponding Cs-vapor pressure at saturation. By stepwise increasing the Cs-temperature up to 420°C the sorption branch of the isotherm "saturation loading-saturation pressure" was obtained. By the same procedure and stepwise decreasing of the Cs-temperature down to about 150°C the desorption branch was tracked, resulting in a complete sorption-desorption cycle for a powder temperature of 800°C. Then the powder temperature was decreased stepwise by 50°C, down to 600°C, and for each step one or more sorption-desorption cycles were performed, one after the other. Afterwards the powders were loaded and unloaded at several constant Cs-pressures by a stepwise variation of 50°C of the powder temperature from 600°C to 800°C and back to 600°C (cf the empty rectangles and triangles in the diagrams). The maximum error on the Cs loadings was estimated to be $\pm 20\%$, by summing up all the principle experimental errors (2).

Table 1

Sample	W-10% Ta	Ta, 22 HCST	Ta, 22 HCST
Weight, g	0.237	0.423	0.412
Thermal treatment	ca. 10^{-5} mm Hg 1300°C, 2h	idem	idem
Specific surface $m^2/g \pm 50\%$ after thermal treat.	0.2	0.2	0.2
O ₂ -content, ppm in weight	19,700	5,140	19,200
Cs in pool, g	0.400	0.355	0.320
Specific activity cpm/mgCs, $\pm 11\%$	278	440	326

Table 2

Torr/degree, S = sorption branch, D = desorption branch

°C	W-10%Ta		Ta 5140		Ta 19200	
	S	D	S	D	S	D
595-605	0.02	0.02	-	-	0.02	-
645-655	0.05	0.06	0.02	-	0.03	ca. 0
695-705	0.05	0.08	0.05	ca. 0	0.05	0.01
745-755	0.06	0.17	0.08	0.02	0.09	0.04
795-805	0.11	0.30	0.15	0.05	0.30	0.20

2. W- 10% Ta

The loading isotherms are shown in fig. 1-5. All of them exhibit a strong hysteresis effect. There are no pronounced plateaus. On the sorption branches of most of the isotherms the loadings do not increase with increasing Cs-pressure up to about 0.4 mm Hg. These vertical parts of the curves (less pronounced on the desorption-branches), corresponding to loadings of 30 - 50 mg Cs/g, are an indication for the existence of a compound. A loading of 30 mgCs/g of powder with a specific surface of $0.2 \text{ m}^2/\text{g}$ would correspond in case of physical adsorption to about 200 monolayers, taking as cross sectional area $18 \cdot 10^{-20} \text{ m}^2/\text{atom Cs}$ (1). These high loadings and the long saturation times (up to 4 hours) also lead to the assumption that compound formation occurs.

From the isotherms the Cs-pressures and the corresponding powder temperatures were taken at a constant loading of 100 mg/g and plotted as $\log p$ vs. $1/T$, to obtain the isoterics for both branches, as shown in fig. 6. From their slopes the isosteric heat of formation (1) was calculated to be about 7.2 Kcal/mole for the sorption branch and 24 Kcal/mole for the desorption branch, indicating that the decomposition of a given compound needs a higher activation energy than its formation (hysteresis).

It follows from the 800°C, 750°C and 700°C isotherms that the loadings on the adsorption branches do practically not increase with increasing Cs-pressures between 0.01 and 0.4 mmHg. In order to find out whether these loadings correspond to stable compounds which do not release any Cs at the given temperatures, 11.87 g of the same W-10 % Ta powder was loaded at 800°C with 380 mgCs to produce a final loading of 32 mg/g. The sorption was performed at consecutive Cs-pressures of 0.07, 0.4, 1.8 and 6.2 mm Hg for 1350, 300,

125 and 50 minutes respectively, to obtain at the same time also the loading rate as a function of time and Cs-pressure. When the Cs¹³⁴-activity on the powder became constant after the last sorption step of 50 minutes at 6.2 mm Hg, a final loading of 26.4 mg/g was obtained. This value is in good agreement with the expected one (32 mg/g) and with the initial loading of the sorption branch of the 800°C isotherm in fig. 1. When the powder temperature was increased to 900°C and the Cs-pressure decreased below 0.01 mmHg for 24 h, no Cs-release could be observed, showing thus the stability of the compound. The loading rates were not a function of time, having for each given Cs-pressure a constant value, shown in fig. 7.

3. Ta

This powder had an O₂-content of 5140 ppm, which is about 4 times less than that of the W-10 % Ta. The loading isotherms are shown in fig. 8-12. The amount of sorbed Cs is by a factor of about 2-4 smaller than on the W-10 % Ta powder, leading to the assumption that the Cs-loading depends also on the O₂-concentration. There is a strong hysteresis effect, with closed loops, and there are more or less pronounced plateaus. The vertical parts of the isotherms correspond to loadings of 10, 25, and 45 mgCs/g which are equivalent, with an O₂-content of 5.14 mg/g, to 0.51, 0.21, and 0.11 mgO₂/mgCs. In the Cs-pressure range of 1-10 mm Hg the loadings on the plateaus of the 700°C, 650°C and 600°C isotherms vary by 16 mg/g on average if the pressure changes by 1 mm Hg.

The isosteres for a loading of 20 mg/g are shown in fig. 13. From their slopes the values of 37 Kcal/mole for the sorption branch and 47 Kcal/mole for the desorption branch were obtained for the respective isosteric heats of formation.

In order to check on the above assumption (loadings depend on O_2 - content) a sample of the same powder was preoxidised in a thermobalance (4 hours, 375-378°C, 0.1 mm Hg of O_2 -pressure) to contain, after heat treatment, 19200 ppm O_2 . Since the solubility of O_2 in Ta below 900°C is reported to be less than about 1000ppm (4), the O_2 is supposed to form a Ta_2O_5 -layer. The presence of Ta_2O_5 in the powder was, after thermal treatment, confirmed by X-ray analysis. The isotherms are shown in fig. 14-18. The quantity of sorbed Cs is by a factor of 4-6 higher than on the Ta-powder which contained roughly 4 times less O_2 . There is a strong hysteresis effect with closed loops and more or less pronounced plateaus. The vertical parts of the isotherms correspond to loadings of 60, 115, and 200 mg/g, which are equivalent, with an O_2 -content of 19.2 mg/g, to 0.32, 0.17 and 0.096 mg O_2 /mgCs. In the Cs-pressure range of 1-10 mm Hg the loadings on the plateaus generally vary by 10-50 mg/g for a pressure change of 1 mm Hg.

The isosteres for a loading of 100 mg/g are shown in fig. 19. From their slopes the values of 28 Kcal/mole for the sorption branch and 63 Kcal/mole for the desorption branch were calculated.

After the experiment the powder was left at 700°C for 42 days, then some points on the isotherm were measured again (fig. 16, asterisks). The sorption characteristics did practically not change.

4. Discussion

- 1) The results of the experiments show that the Cs-loadings are proportional to the amount of O_2 present on the powders in form of a Ta_2O_5 -layer. This oxide, can be

considered stable, since the pre-oxidised Ta powder had lost less than 4 % of its O_2 due to a thermal treatment of 2 hours at $1300^\circ C$ in a vacuum of about 10^{-5} mm Hg. Each of the three powders had irreversible loadings at low Cs-pressures, i.e., about 30 mg/g for the W-10 % Ta powder (19700 ppm O_2), 10 mg/g for Ta (5140 ppm O_2), and 60 mg/g for Ta (19200 ppm O_2).

The observed hysteresis effect is due probably to different activation energies for the formation and decomposition of a given compound.

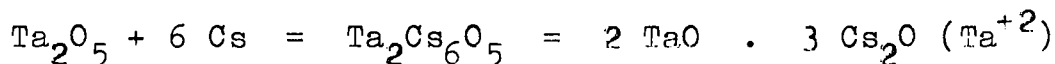
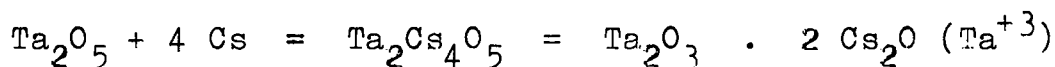
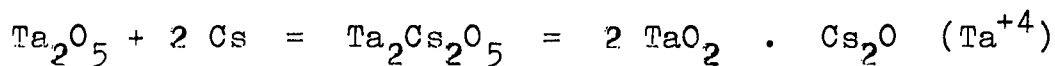
- 2) Generally on the plateaus of the Ta-isotherms, which could be of interest for converter operation, the Cs-loadings vary between 10 and 50 mg/g when the Cs-pressure changes by 1 mm Hg. The Cs-pressure variations per $^\circ C$ at several powder temperatures were obtained from p-T plots and are shown in table 2, including also the data for W-10 % Ta.

The Ta-Cs reservoirs should, to avoid hysteresis, operate on the desorption branches of the plateaus which are situated within a Cs-pressure range of 1 to 10 mm Hg. Two general cases can be distinguished :

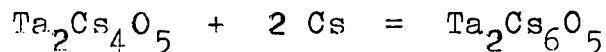
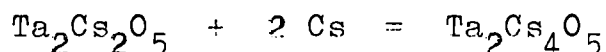
- a) If in a converter Cs-losses occur at a constant reservoir temperature the loadings and the Cs-pressures will decrease as indicated by the isotherms. When starting from the sorption branch, there will be a transition to the desorption branch.
- b) If there are no Cs-losses and the reservoir temperature varies, the Cs-pressures will change as indicated by the isosteres. No transition will occur from the sorption to the desorption isostere.

When Cs-losses occur and the reservoir temperature changes simultaneously, combinations of the cases a) and b) will result. By means of the corresponding isotherms and isosteres the Cs-pressure variation can be estimated.

- 3) The ratios mgO_2/mgCs are similar for both Ta powders. The shapes of the isotherms indicate the existence of three compounds, corresponding to ratios of 0.32, 0.17, and 0.10 $\text{mg}/\text{O}_2\text{mgCs}$. From these values a stoichiometric composition of $\text{CsO}_{2.66}$, $\text{CsO}_{1.41}$, and $\text{CsO}_{0.83}$ or $\text{Cs}_2\text{O}_5^{-8}$, $\text{Cs}_4\text{O}_5^{-6}$, and $\text{Cs}_6\text{O}_5^{-4}$ is obtained respectively. Assuming that the Ta-valence decreases with increasing Cs-loading by steps of 1, the following compounds can be derived :



The intermediate transitions can be described by :

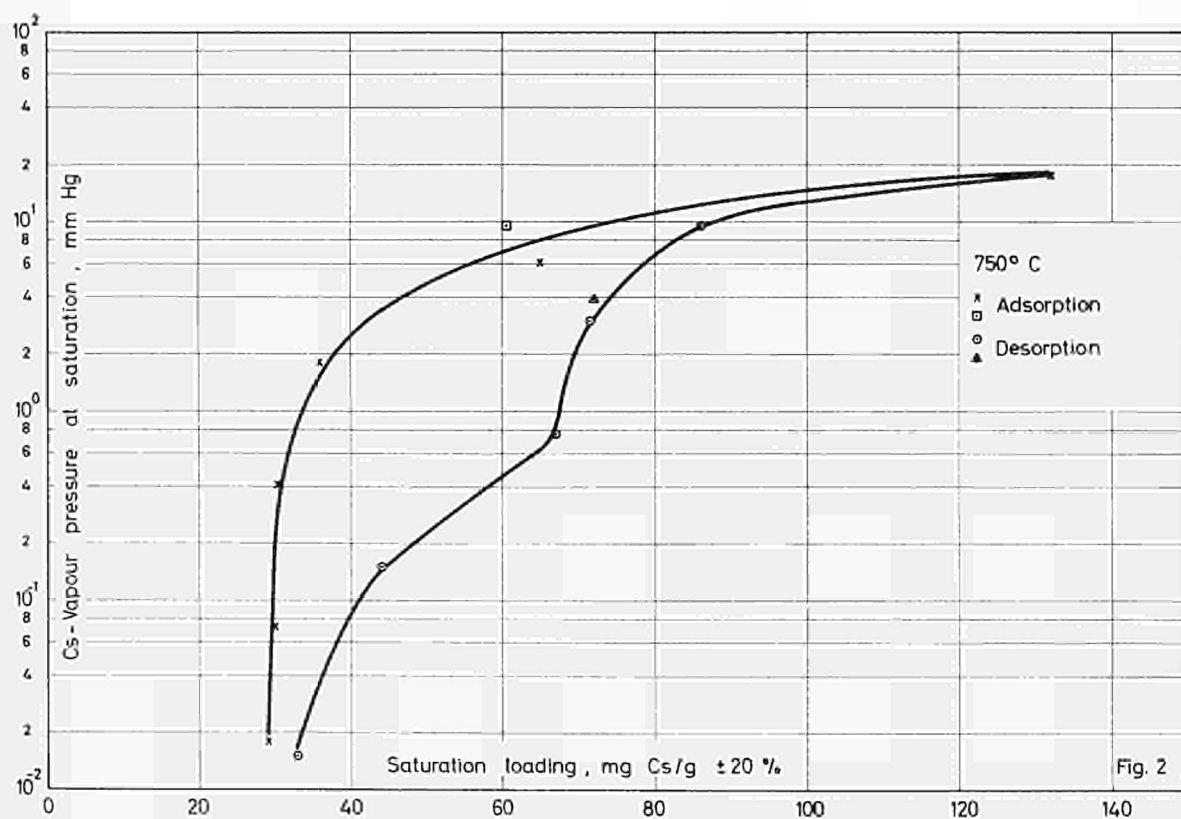
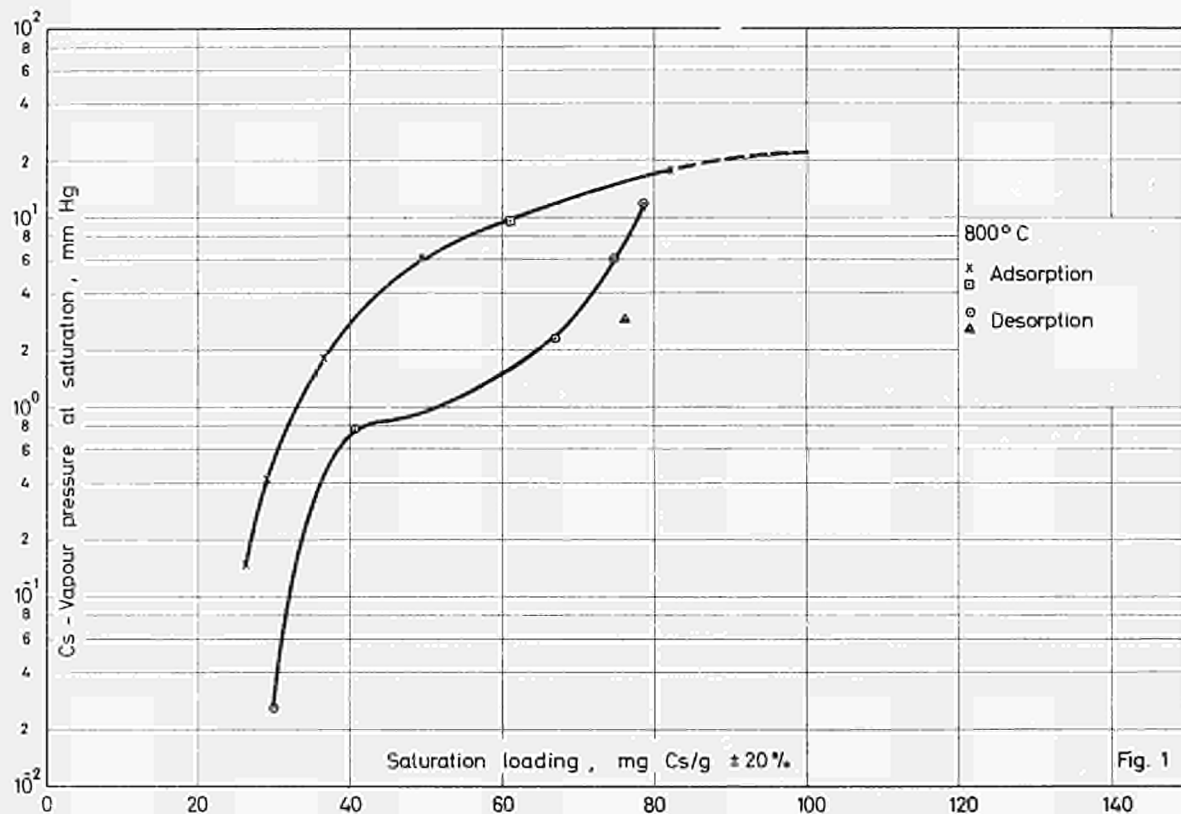


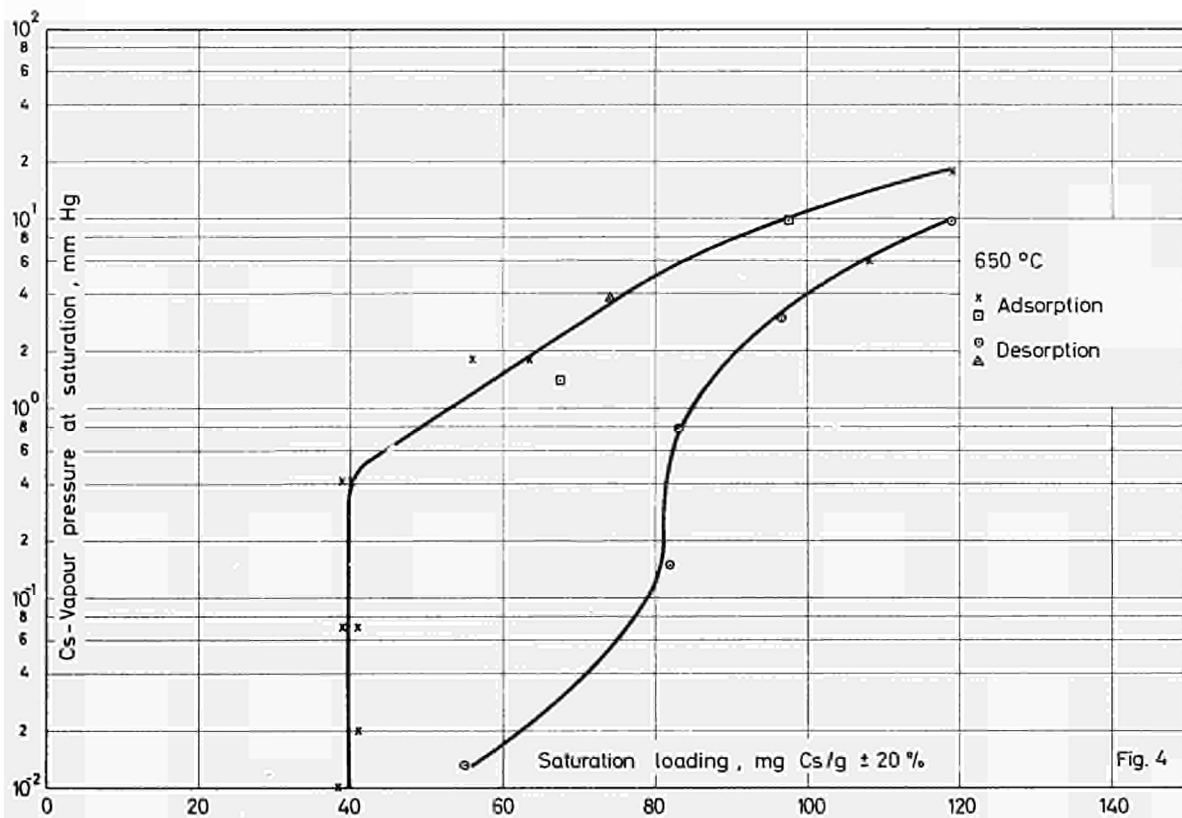
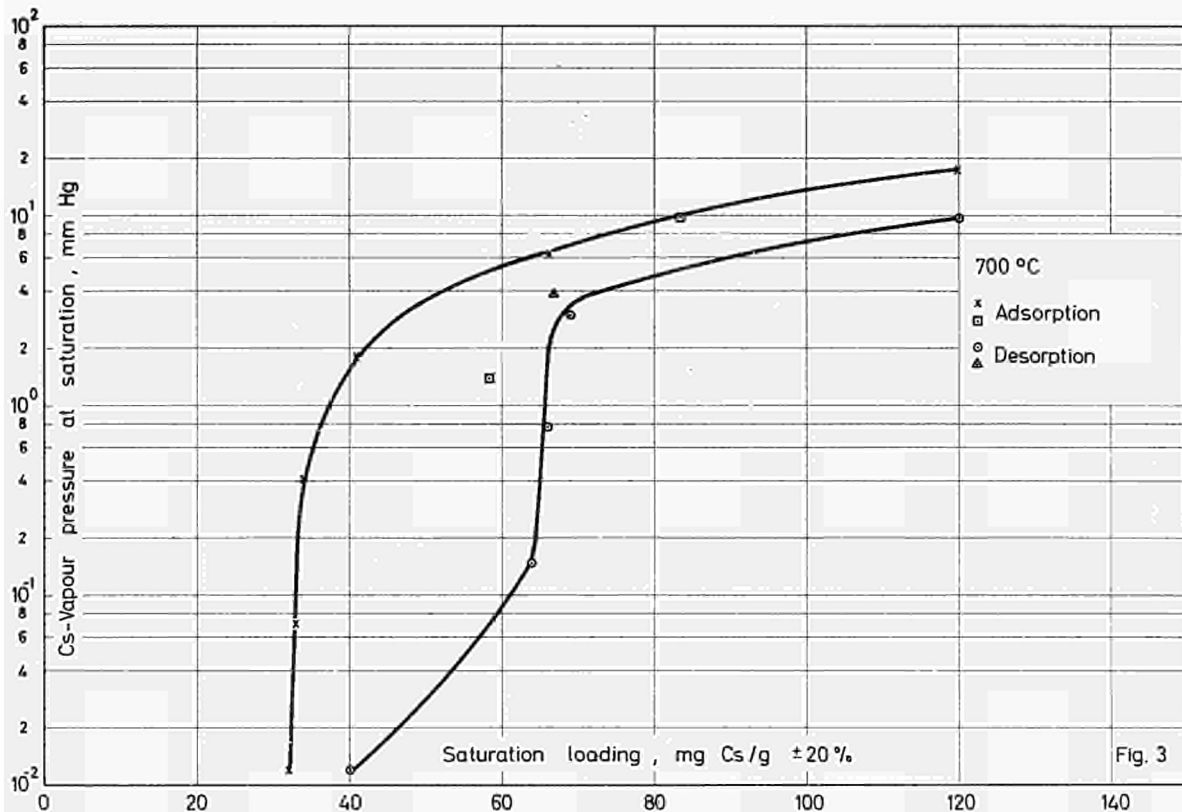
The existence in vacuum of a 5-valent, anhydrous, X-ray amorphous $\text{Ta}_2\text{O}_5 \cdot \text{Cs}_2\text{O}$ was already reported (5). A further development of reservoirs, based on these results, would consist in preparing Ta_2O_5 in a more convenient form than powders for practical converter application, e.g. as sintered pellets, and to determine the p-T-L characteristics.

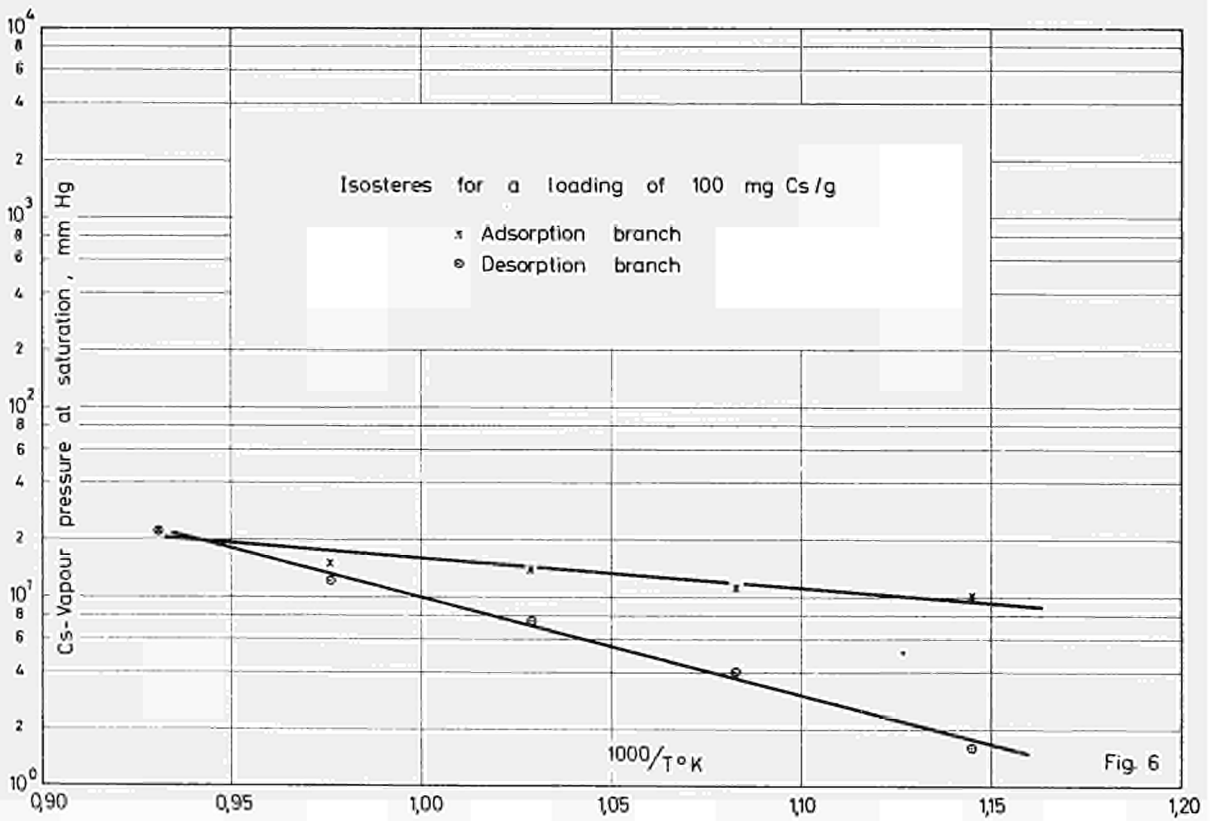
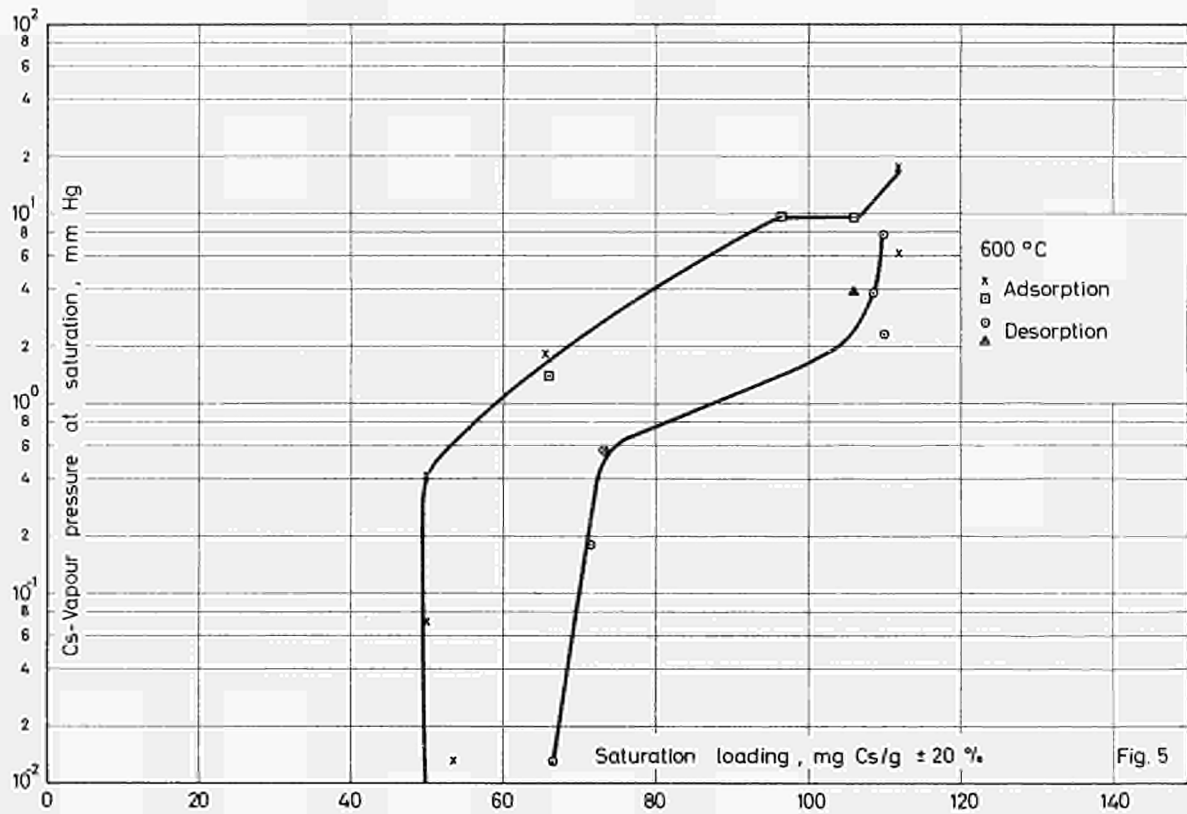
Useful discussions on this work by Dr. A. BUSSE, Materials Division, are gratefully acknowledged.

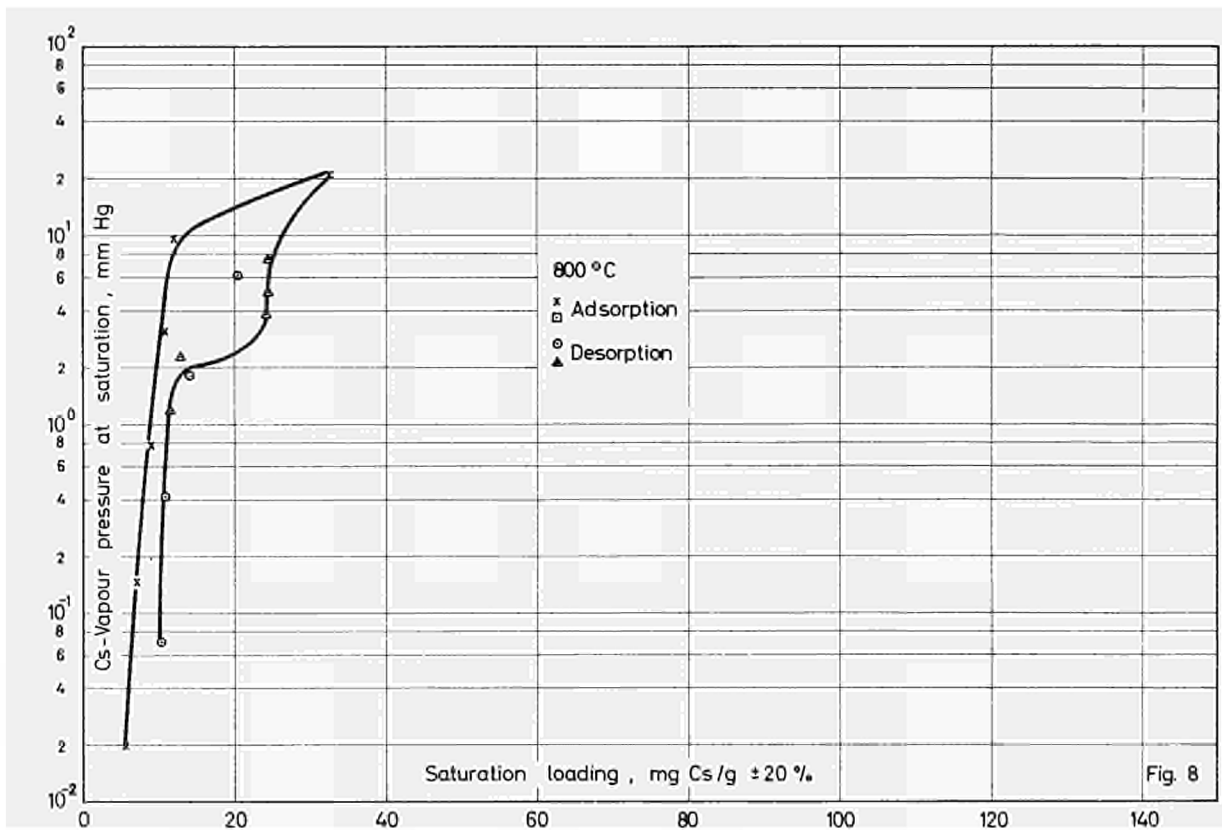
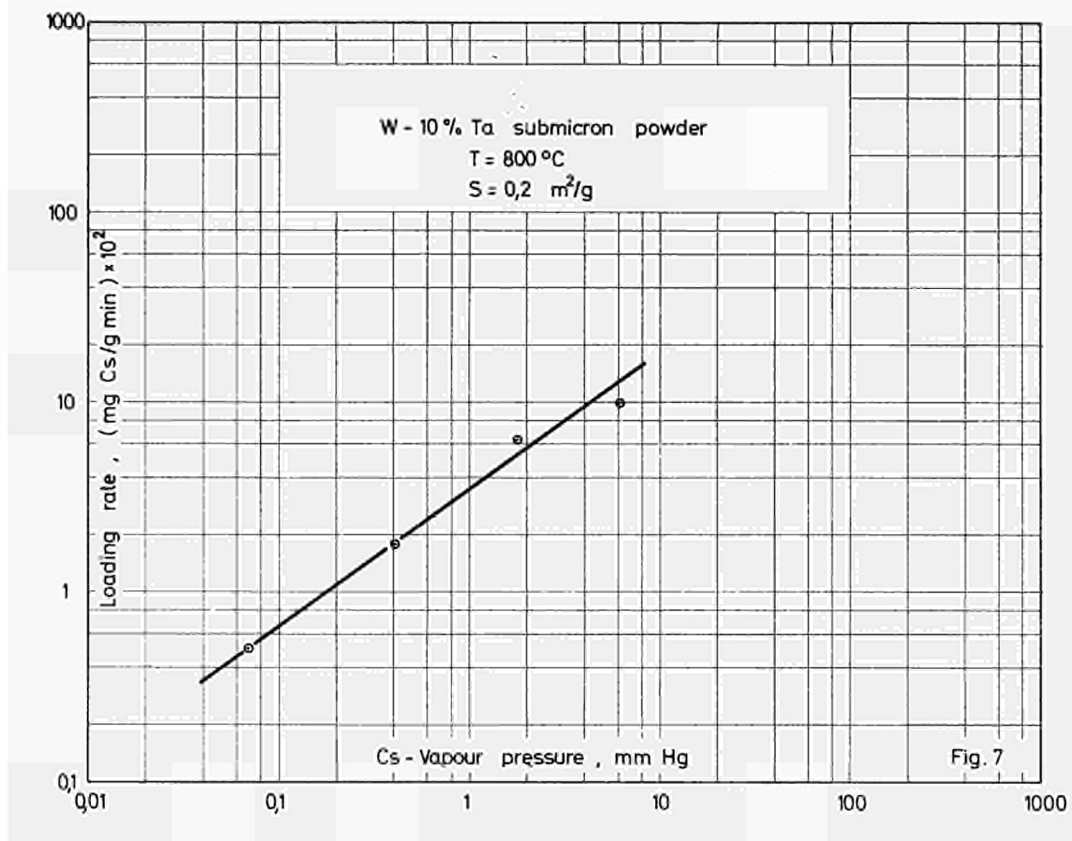
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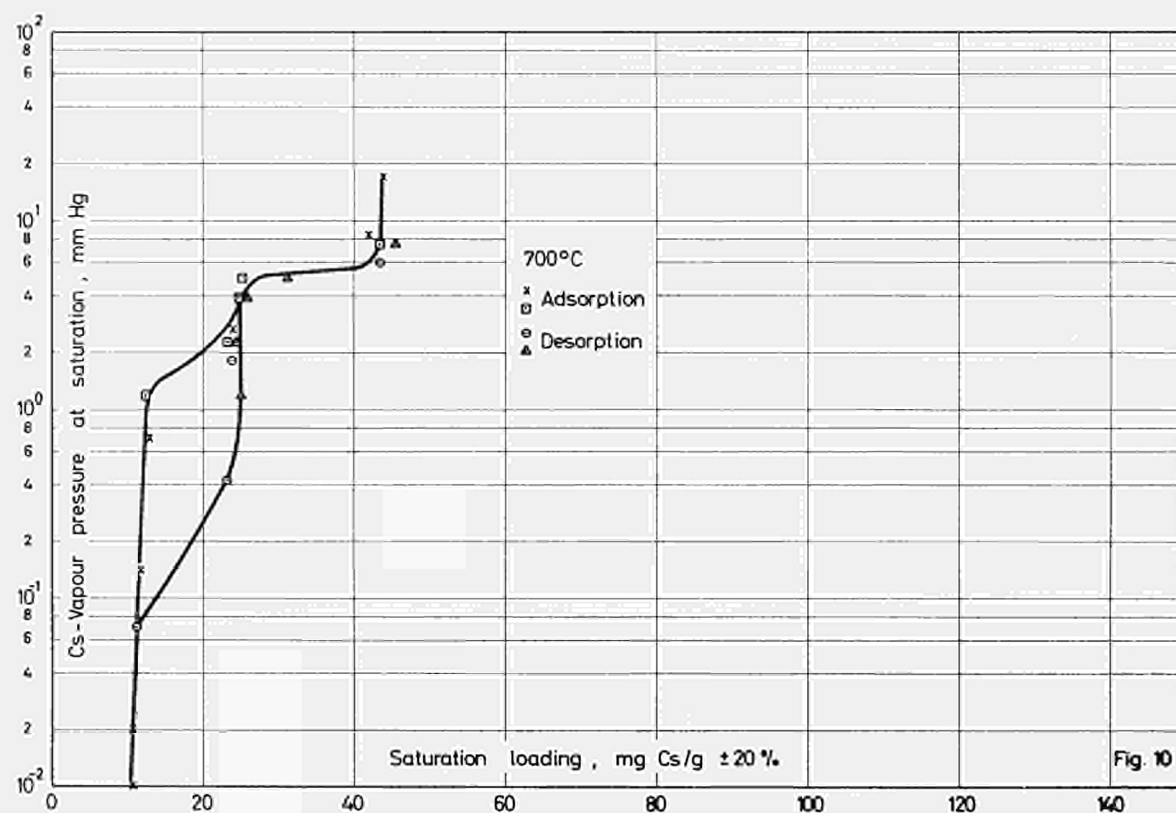
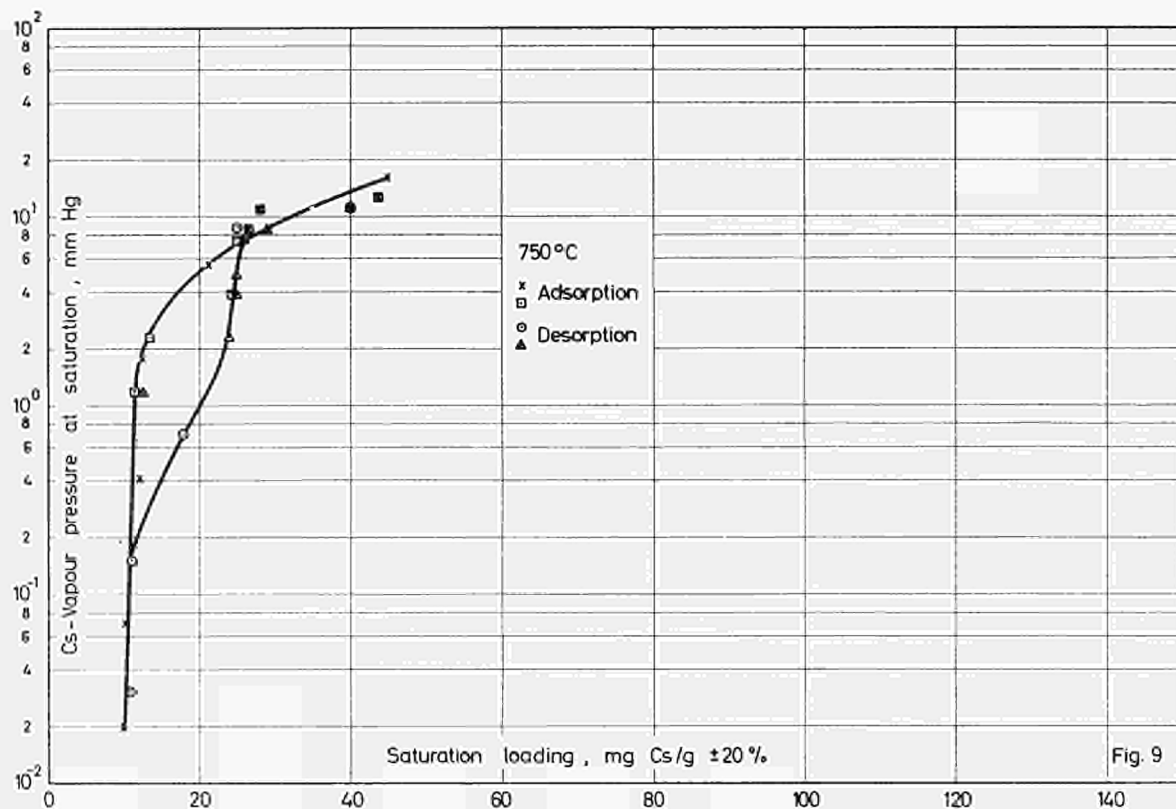
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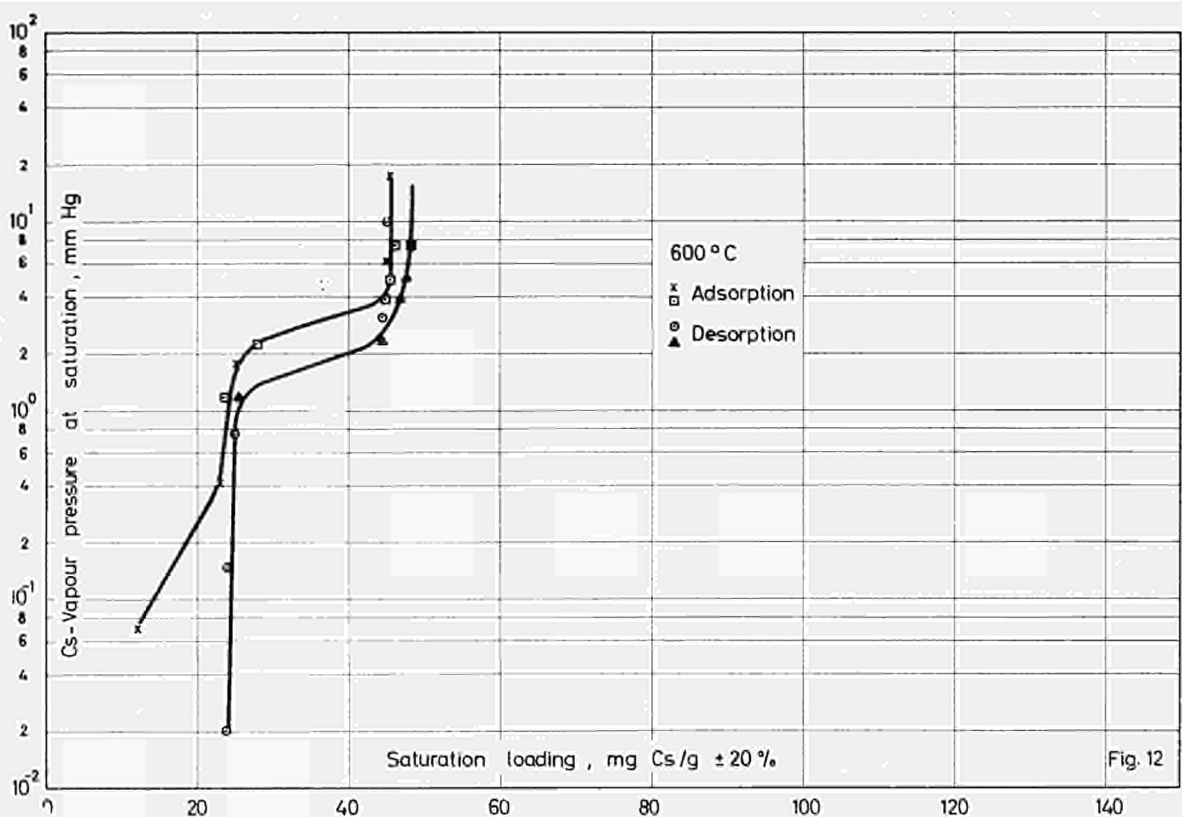
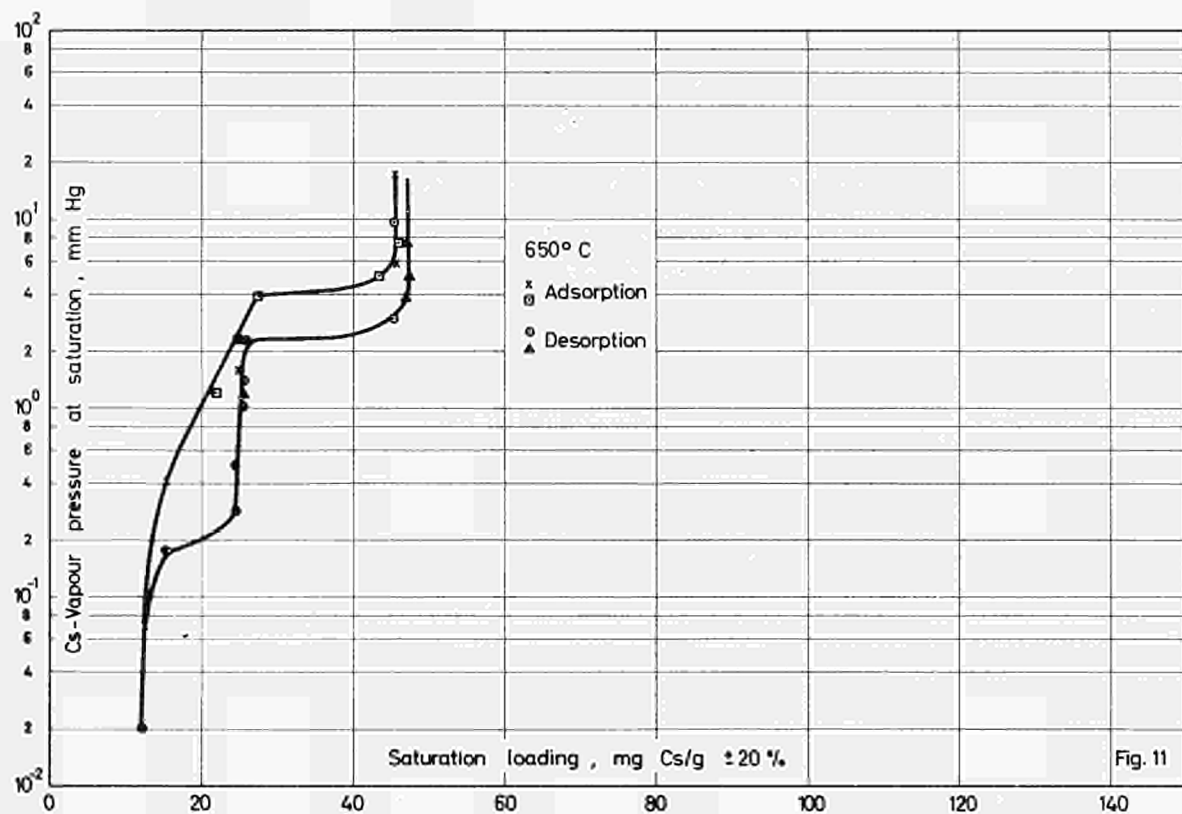


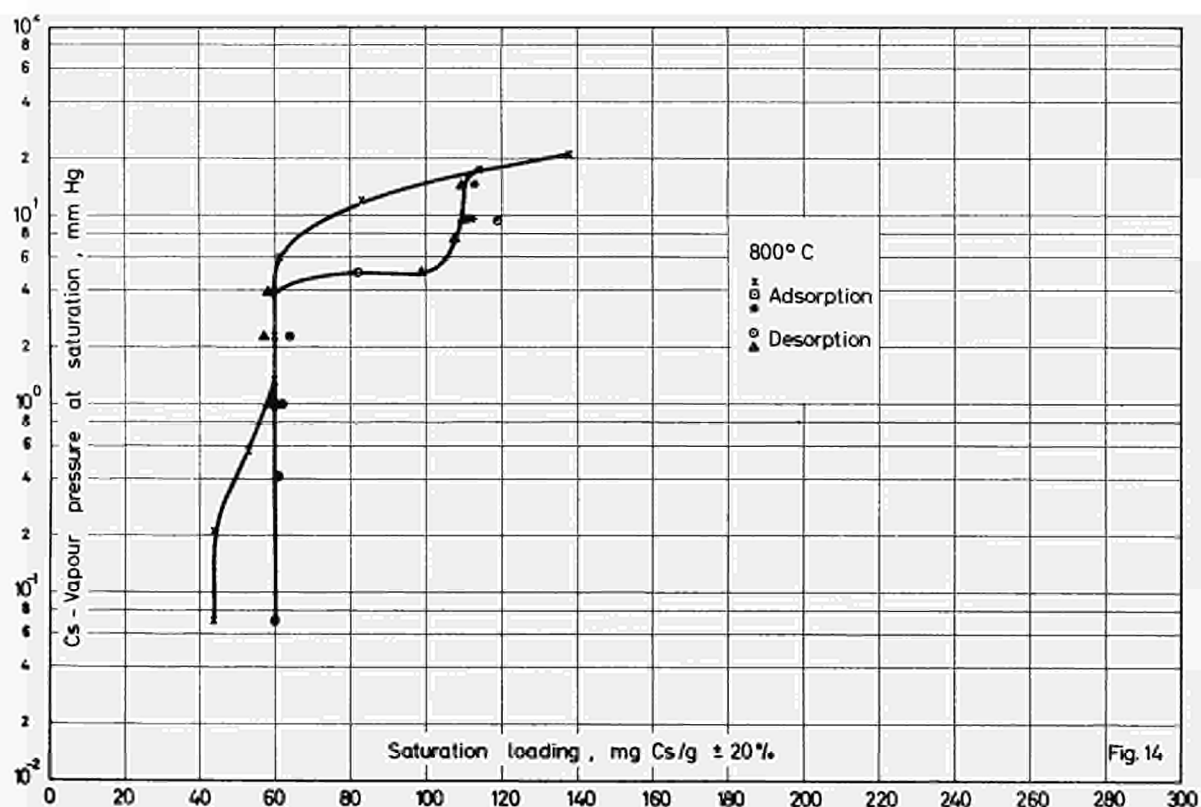
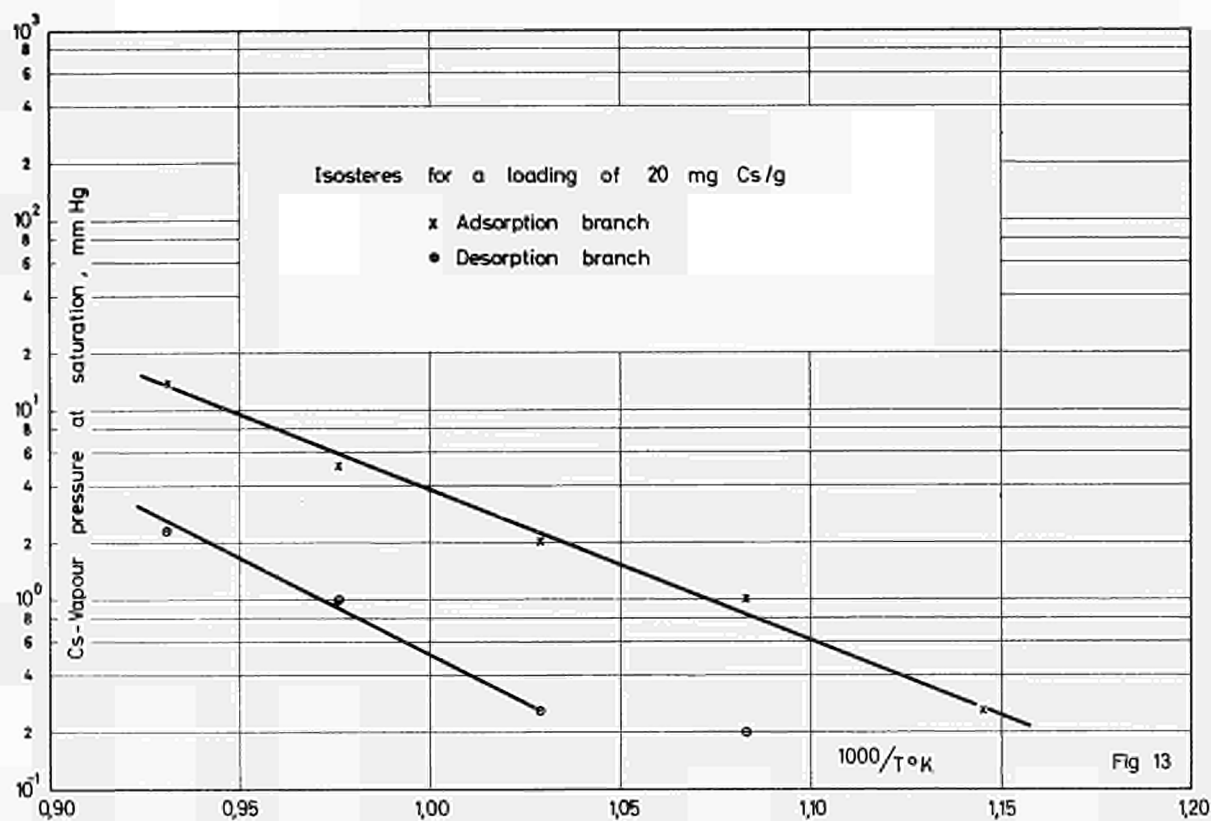


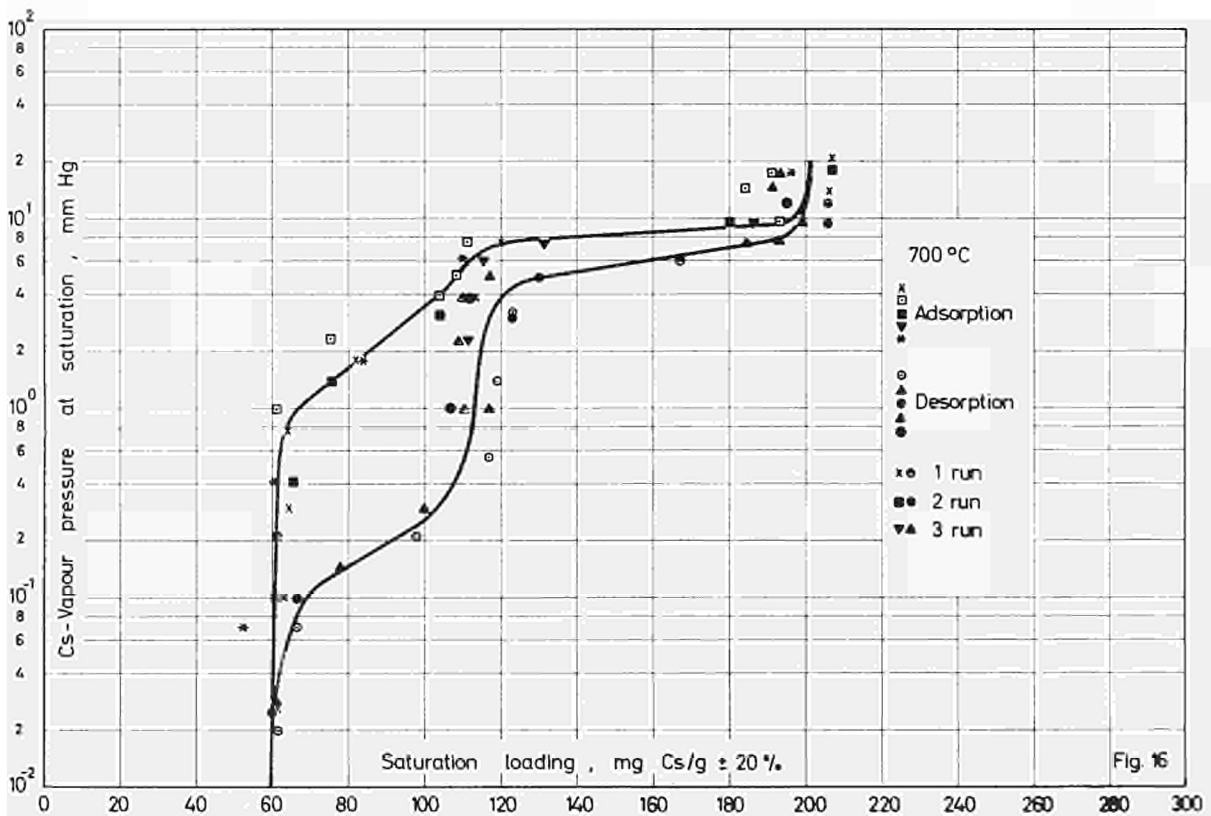
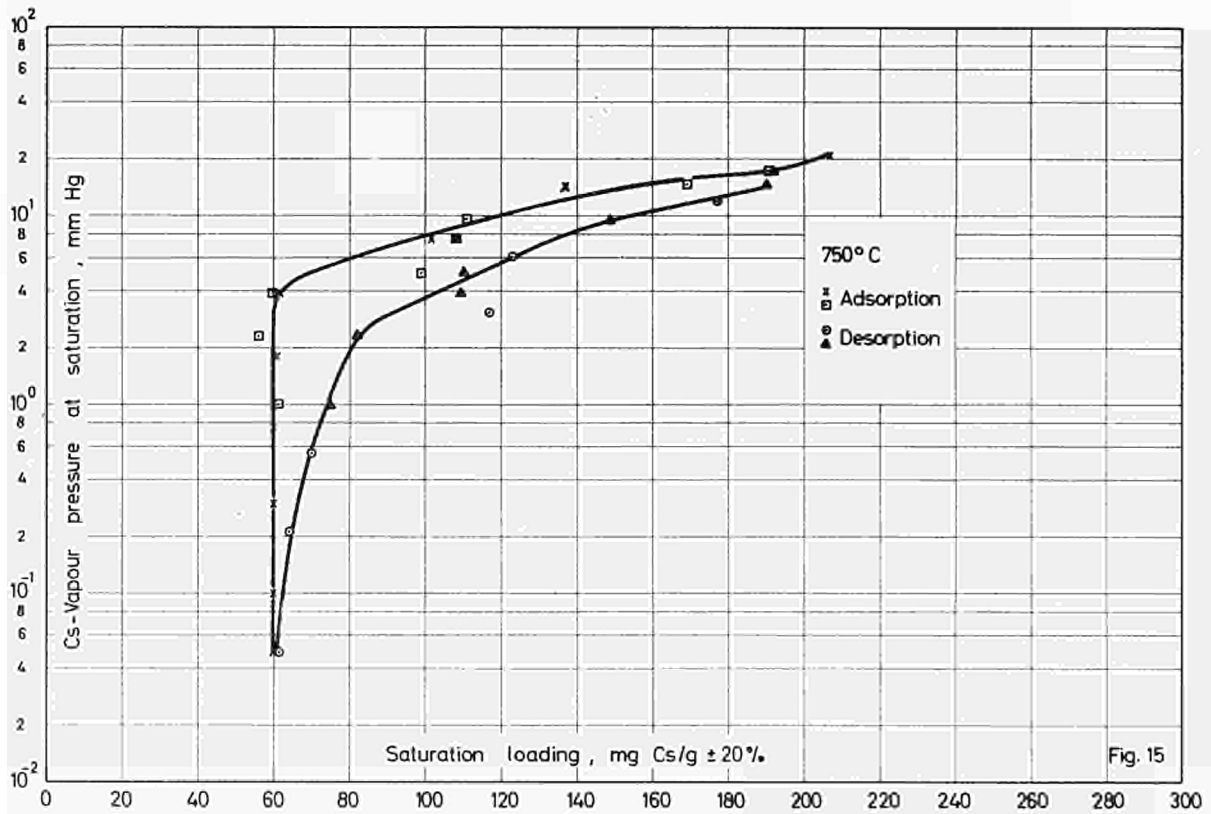


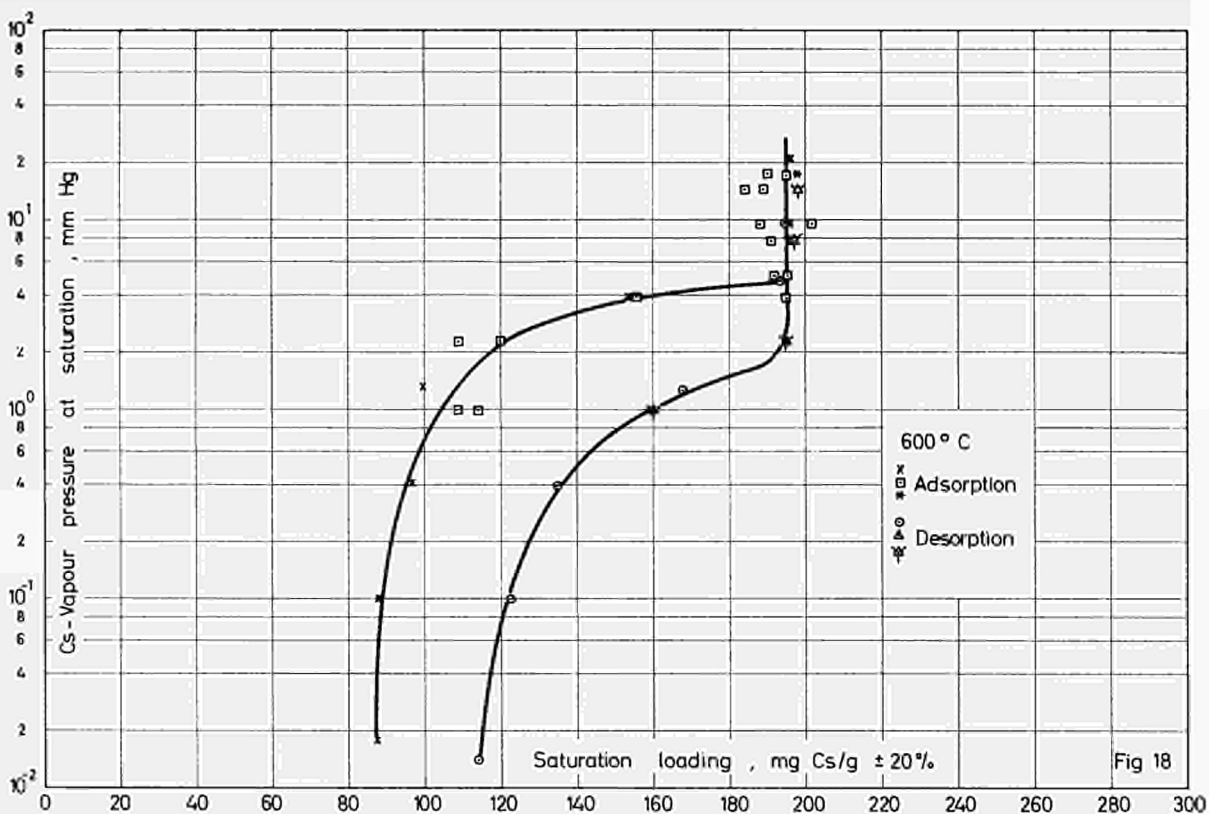
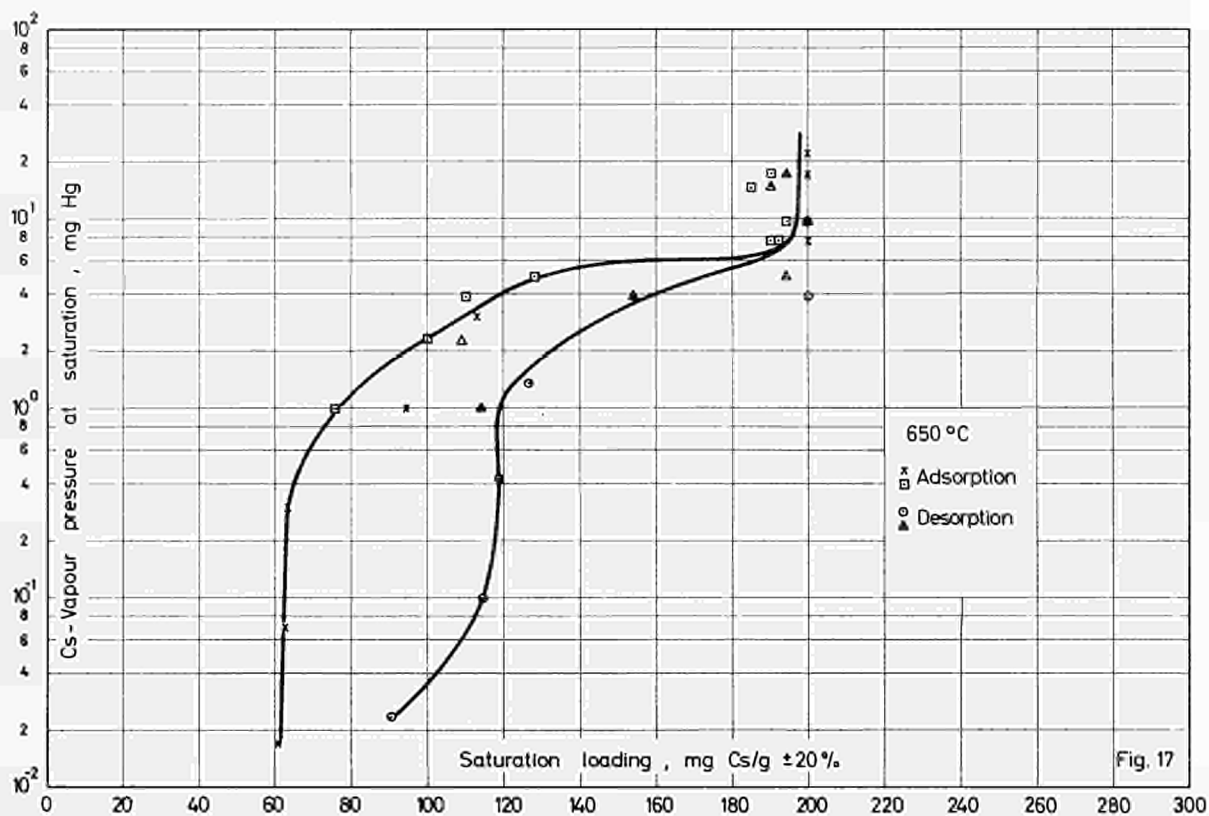


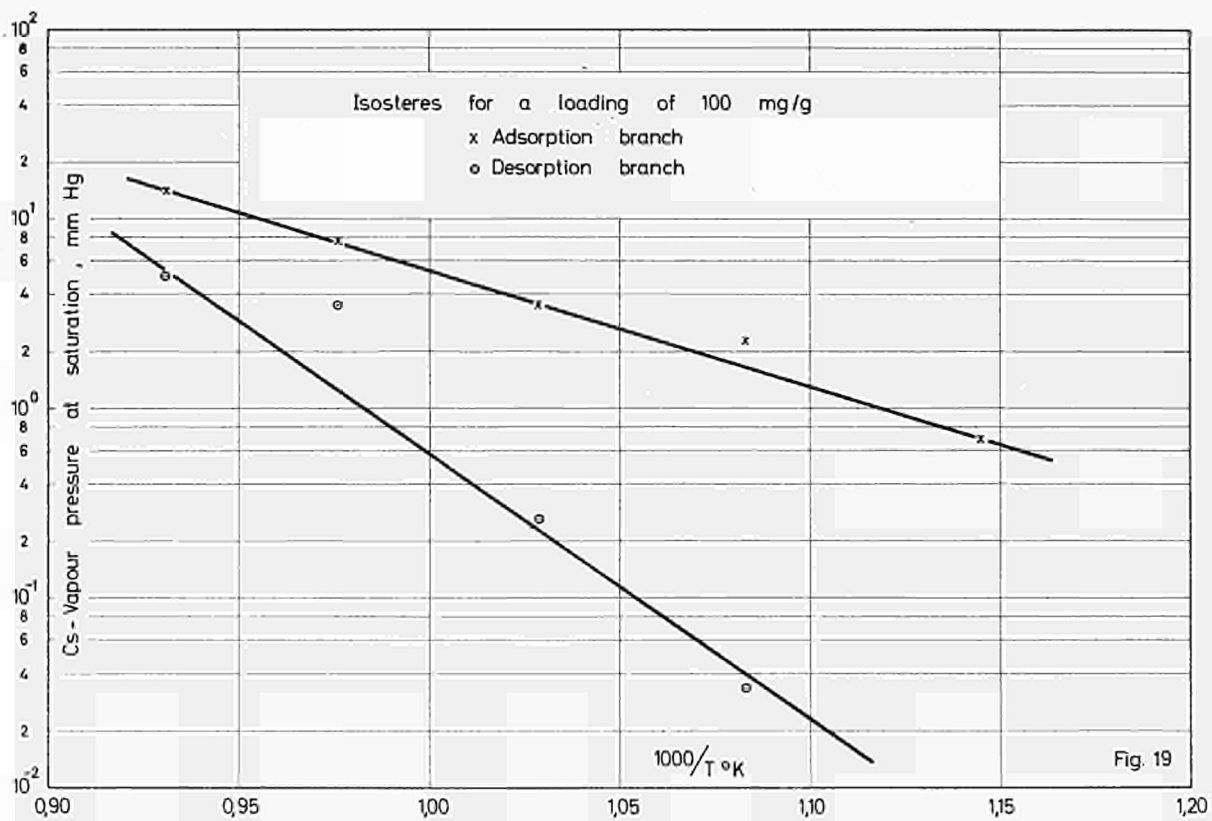












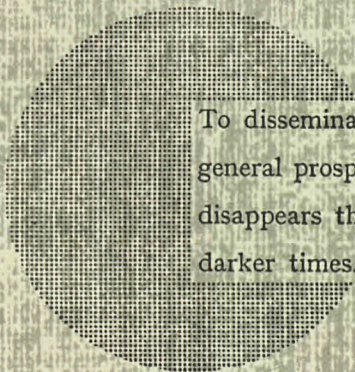
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