

INFLUENCE OF PETROLEUM COKE SULPHUR CONTENT ON THE SODIUM SENSITIVITY OF CARBON ANODES

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ABSTRACT

Carbon anodes can contain significant quantities of sodium depending on the raw materials and recycled butts cleanliness. The extent of the catalytic effect of the sodium on the anode reactivity, i.e. the "sodium sensitivity", is dependant on the coke nature.

An investigation of a range of petroleum cokes was undertaken to study the influence of the sulphur on the sodium sensitivity. Besides the standard characterisation tests, a range of analytical methods was employed including Controlled Atmosphere Electron Microscopy (CAEM), X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS) and Thermogravimetric Analysis (TGA).

The results of these investigations have been used to elucidate a mechanism to explain the sodium sensitivity. A short video showing the contrasting behaviour of two cokes at the microscopic level will be shown.

INTRODUCTION

The raw materials used for the production of the dry recipe in prebaked anode plants are petroleum coke, crushed butts, green scrap and baked scrap. A binder, typically coal tar pitch, is added to coat the filler aggregate particles and ensure the compacted anode block maintains its structural form.

Carbon anodes can contain significant quantities of sodium depending on the raw materials and recycled butts cleanliness. Sodium can be inherent in crude oil, or acquired during the drilling procedure. During oil refining and coking, the majority of the metals are deposited in the coke. Further sodium can be deposited on the coke while decoking the drum and after calcining if the purity of the water used for the cutting and cooling operations is not controlled.

Prior to tar distillation for pitch production the feedstock is dosed with controlled amounts of either a sodium carbonate or sodium hydroxide solution to neutralise ammonium chloride dissolved in the tar water¹. This eliminates the

problem of corrosion in the fractionating equipment due to chloride attack. Unfortunately the added sodium ends up in the pitch and subsequently the anode.

Spent anode butts are removed from the cell, washed and crushed before mixing with the pitch and coke to form the anode. A large level of the impurities present in the anode is concentrated in the butts. Butts may also contain impregnated cryolite (Na_3AlF_6) and bath material (a mixture of cryolite and alumina Al_2O_3) depending on the efficiency of the washing procedure. Dirty butts may contain as much as 12000 ppm sodium.

The extent of the catalytic effect of the sodium on the anode reactivity, i.e. the "sodium sensitivity", is dependant on the coke nature. R&D Carbon Ltd developed a bench scale procedure to quantify this which was presented in Light Metals 1991². Figure 1 shows the influence of increasing sodium (dirty butts) content on the carboxy reactivity residue of full size anodes made out of two different petroleum cokes.

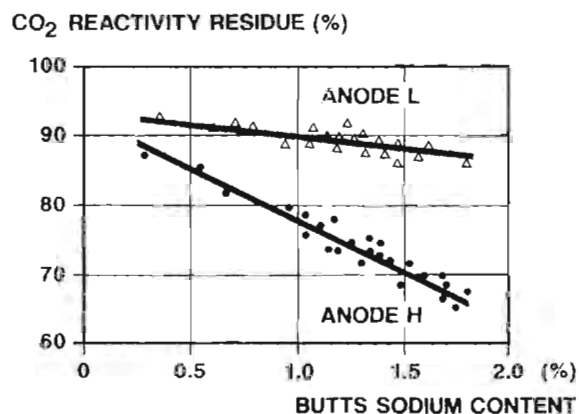


Figure 1. Influence of the butts sodium content on the carboxy reactivity residue of anodes.

There is a strong indication that the sensitivity of the cokes to dirty butts addition (i.e. their sodium sensitivity) is different. The photograph in figure 2 illustrates the large differences that can occur in anodes made with cokes having a similar granular carboxy reactivity.

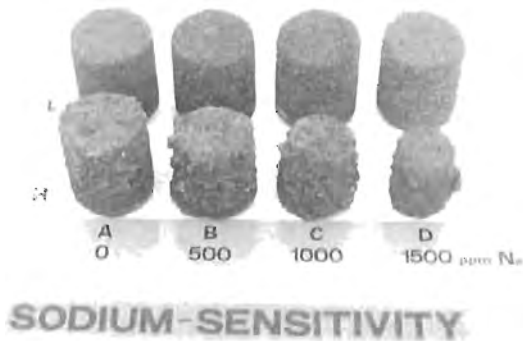


Figure 2. The carboxy reactivity residues of high and low sodium sensitivity cokes.

A comparison of the results of many such investigations led us to believe that the petroleum coke sulphur content had an important influence on the sodium sensitivity (other important parameters include the coke porosity, calcination degree and macrostructure). An investigation of two petroleum cokes with high or low sulphur but otherwise similar characteristics was undertaken to study the influence of the sulphur content. Besides the standard characterisation tests, a range of analytical methods were employed.

BENCH SCALE PROCEDURE

Bench scale electrodes containing increasing levels of sodium contamination were prepared according to the procedure of Fischer and Perruchoud². The bench scale results for typical low (labelled M) and high (labelled S) sulphur cokes are shown in figures 3 and 4 respectively.

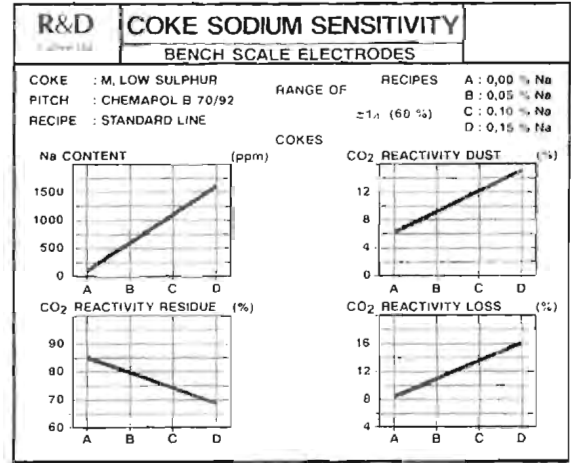


Figure 3. Bench Scale results for low sulphur coke M.

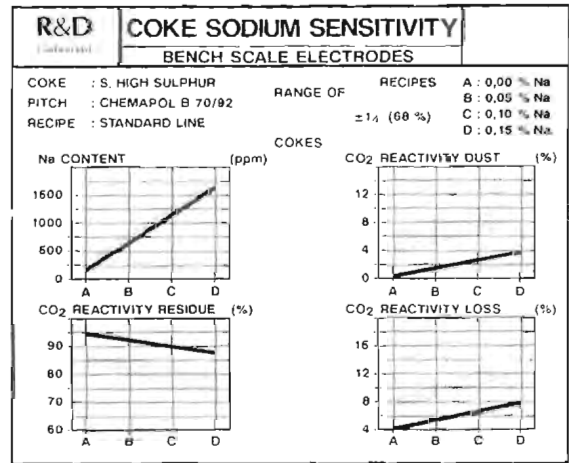


Figure 4. Bench scale results for high sulphur coke S.

It is evident that the sensitivity to sodium additions is much greater for coke M, i.e. the catalytic activity of the sodium is much greater in the absence of sulphur.

Thermogravimetric Analysis (TGA)

A Stanton Redcroft fully automated thermobalance was used to measure the carboxy reactivity of the calcined petroleum cokes and corresponding cryolite contaminated binder matrix electrodes. Binder matrix electrodes are prepared using only the dust fraction in the dry aggregate³. In the case of analyzing small contaminated samples, using binder matrix electrodes enabled a more homogeneous contamination and therefore more reproducible results. A 100mg sample of crushed material (grain size 1–1.4mm) was heated at a rate of 1°C/min in an atmosphere of flowing (21mL/min) carbon dioxide from 550°C until a 90% weight loss was obtained.

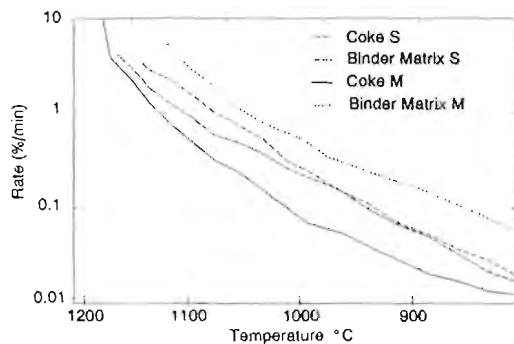


Figure 5. Arrhenius plots of carboxy reactivity.

The results are presented in the form of Arrhenius plots in figure 5. In the case of the low sulphur coke M, the granular coke material shows a low reactivity and slow reaction rate. When electrodes are prepared from this coke contaminated with cryolite, the reaction profile changes significantly. The onset of reaction is approximately 100°C lower and therefore the rate of reaction is faster at any given temperature. This difference is attributed to catalysis of the carboxy attack by sodium. The situation for the high sulphur coke S however is quite different. The reaction profile of this coke is relatively unchanged when electrodes contaminated with cryolite are prepared. The onset of gasification is at the same temperature (~800°C) and the reaction rate at any particular temperature is similar. Here it appears that the catalytic activity of the sodium has been inhibited.

Secondary Ion Mass Spectrometry (SIMS)

SIMS⁴ is an analytical technique that can be used to characterise the surface and near surface region of solids. The technique uses a beam of energetic (0.5 – 20 keV) primary ions to sputter the sample surface, producing ionised secondary particles that are detected using a mass spectrometer. In addition an image can be formed using a focused ion beam (in a manner analogous to that of the electron beam in SEM) and in this way element specific maps or images can be generated. A schematic overview of the technique is shown in figure 6.

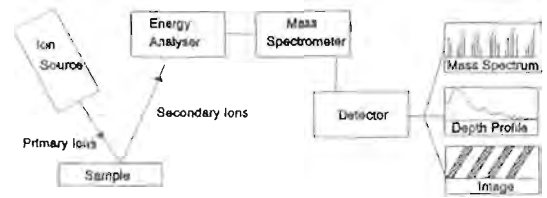


Figure 6. Schematic diagram of Secondary Ion Mass Spectrometry (SIMS).

In electrodes made from petroleum coke and coal tar pitch, element maps can be used to study the distribution of impurities within the electrode. As vanadium is present predominantly in petroleum coke and not in pitch, and zinc is present predominantly in pitch but not petroleum coke, a comparison of the sodium distribution with the distributions of these elements can provide information on the mobility of sodium.

Figure 7 shows element distribution maps for baked bench scale electrodes prepared from cokes low and high in sulphur. For the low sulphur material, the sodium distribution is throughout the entire material, showing no preference for the coke or pitch phase and suggesting that the material is highly mobile. In the high sulphur material the sodium distribution is coincident with the petroleum coke phase. This is suggestive of a strong interaction between the sodium and a coke impurity (sulphur) which binds the sodium to the coke and thus prevents further migration and catalysis.

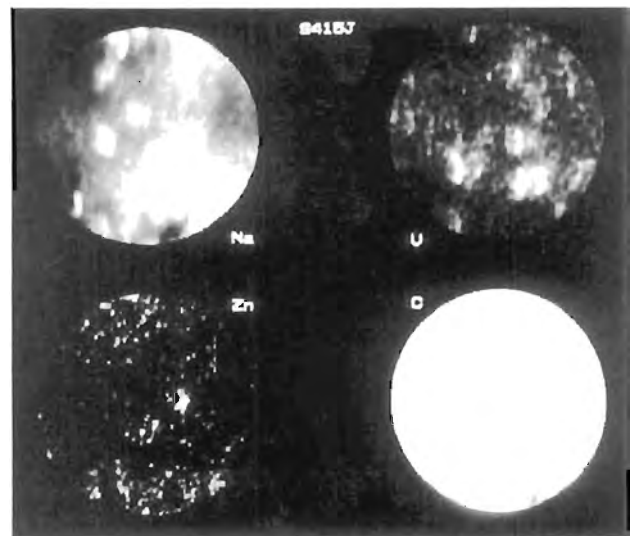


Figure 7A. SIMS element distribution maps (diameter 150µm) for electrode containing low sulphur coke M.

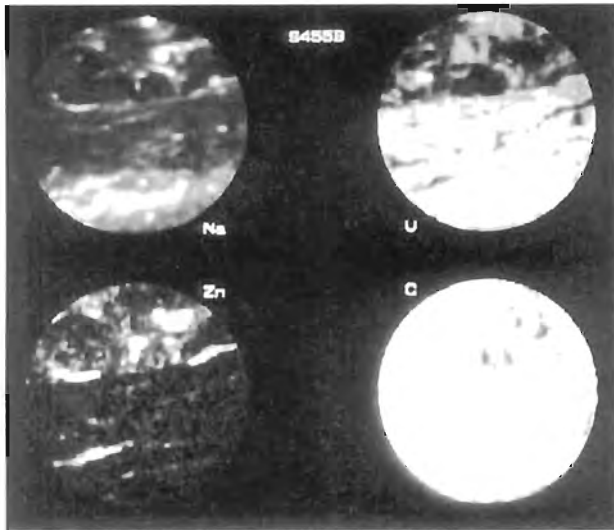


Figure 7B. SIMS element distribution maps (diameter $150\mu\text{m}$) for electrode containing high sulphur coke S.

Controlled Atmosphere Electron Microscopy (CAEM)

Controlled atmosphere electron microscopy (CAEM)⁵ is an *in situ* scanning transmission electron microscopy technique. By a clever design adaptation, it overcomes the principle limitation of conventional transmission electron microscopy, ie. a vacuum condition, and thus allows direct observation of the changes taking place in a transmission specimen as it is heated in the presence of a gas.

The advantage of such a technique is that the investigator is not required to remove the specimen from the reaction environment over periods of time to collect comparative micrographs, and so the associated problems of specimen cooling, contamination and subsequent relocation of the region of interest are overcome. A simple schematic diagram of the microscope is shown in figure 8.

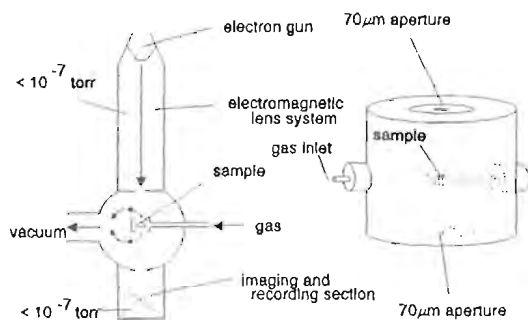


Figure 8. Schematic of the Controlled Atmosphere Electron Microscope.

Sections of the electrodes were carefully ground down to sizes of the order of $100\mu\text{m}$ using a dry grinding procedure with a diamond saw to avoid contamination of the specimen. These fragments were then ultrasonically dispersed in *n*-butanol. A drop of this suspension was applied to a transmission specimen of single crystal graphite support mounted on a stainless steel microscope grid. This combination was placed in the heating stage and inserted into the environment cell located in the specimen chamber of the microscope. Specimens were then reacted in the presence of 0.3 Torr of carbon dioxide.

Two series of transmission electron micrographs taken during the course of a reaction are shown in figures 9 and 10 for low and high sulphur coke respectively. The behaviour of the two materials is significantly different.

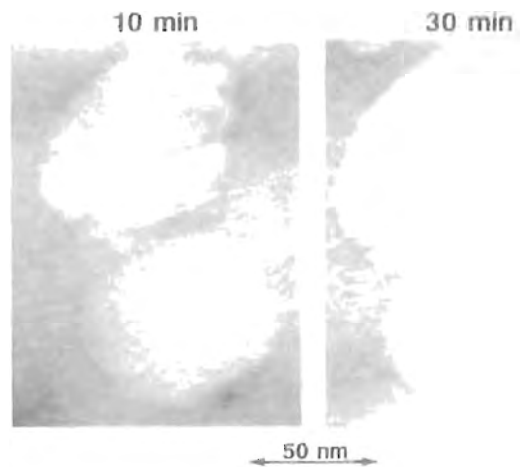


Figure 9. Transmission electron micrographs of low sulphur petroleum coke in CO_2 .

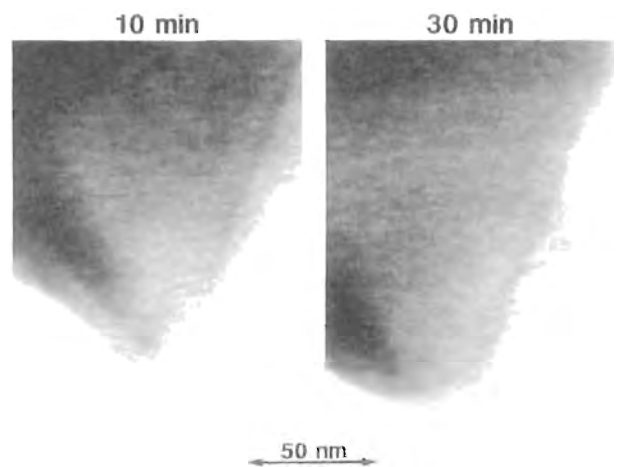


Figure 10. Transmission electron micrographs for high sulphur coke in CO_2 .

In the low sulphur material, the catalytic attack of the sodium derived from cryolite is extremely high. Particle nucleation and the associated formation of tiny pits occurs at an activation temperature as low as 200°C (depending on the heating rate). The onset of gasification occurs following nucleation, occurring by an edge recession mode which is characteristic of a metal oxide species, and continues until all the carbon has been consumed.

In the presence of sulphur this catalytic activity is completely inhibited. No catalytic activity is observed and gasification does not occur before a temperature of 860°C, which is considered to be uncatalysed gasification. The absence of any visible catalyst signifies that the impurity is not present as a metal oxide but instead in a strongly bound spread state (which is invisible in TEM) and therefore unable to undergo the catalytic oxidation/reduction cycle which is observed with sodium species in the absence of sulphur.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy⁶ is a highly sensitive surface analysis technique used to determine the elemental composition of the outermost atomic layers of a solid and to obtain detailed knowledge about the chemical binding states, surface homogeneity and the state of adsorbates. The basic process involves the adsorption of x-rays by an atom and the subsequent ejection of core or valence electrons. Information about the elements present is extracted from the binding energies of ejected electrons and the related shifts in these energies.

Narrow window scans of the Na1s and S2s regions are shown in figure 11.

A Na auger parameter can be calculated from the binding energies from the following equation:

$$AP = 1254 - BE(\text{NaKLL}) + BE(\text{Na1s})$$

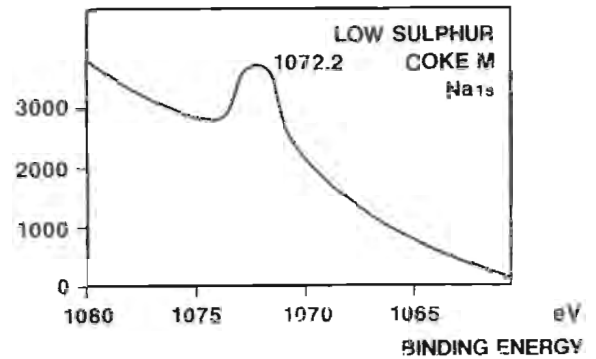
where AP = auger parameter
BE = binding energy

The chemical shifts and auger parameter are tabulated below.

Table 1. XPS data

	Coke S	Coke M
C1s	284.4	284.4
Na1s	1072.7	1072.2
NaKLL	263.9	263.7
AP	2062.8	2062.5
S2s	236.8 / 228.3	236.4
S2p	163.8	164.0

INTENSITY (COUNTS)



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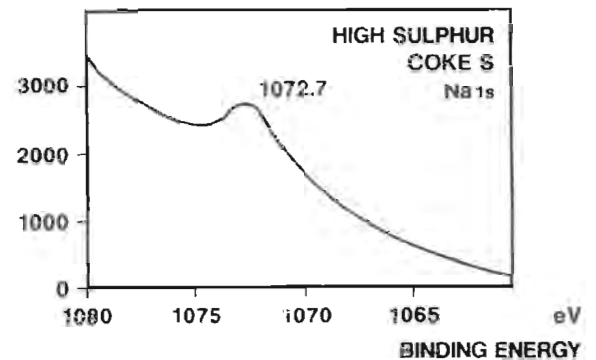
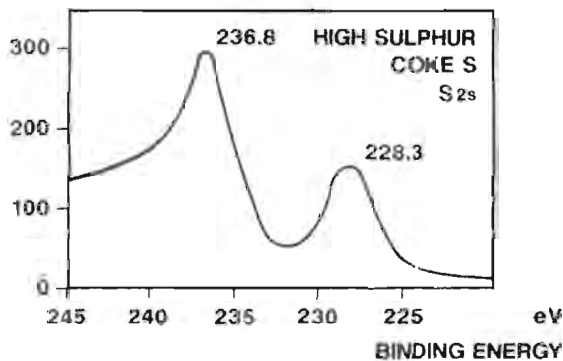


Figure 11A. XPS Na1s narrow scans.

The value of the auger parameter and the shift in the S2p binding energy can be used to identify the chemical state. The Na peaks here are assigned as an oxide or sulphate species, the sulphur peak at ~236.6 shows the presence of sulphate. Of interest is the presence of the second sulphur peak in the high sulphur material which is assigned to elemental S or a carbon sulphide. This peak is not present in the low sulphur material, where all available sulphur appears to be in sulphate form. It is postulated that insufficient sulphur was present to bind all the sodium whereas in the high sulphur material, unbound sulphur is still available to neutralise the catalytic activity. It is believed that the neutralisation takes place during the baking phase of the anode preparation.

INTENSITY (COUNTS)



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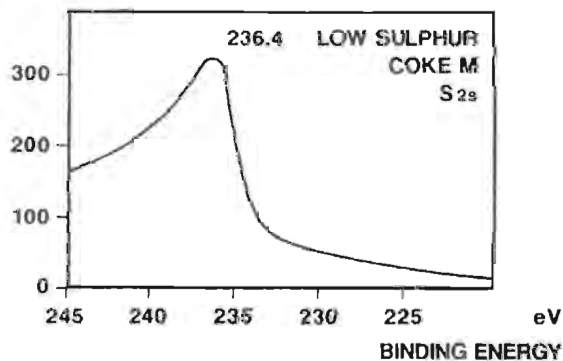
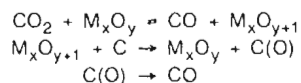


Figure 11B. XPS S_{2s} narrow scans.

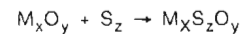
A MODEL FOR THE SODIUM SENSITIVITY

The general mechanism for the catalytic gasification given below was outlined by Moulijn and Kapteijn (1985)⁷, taking into account all the postulated mechanisms in the literature and published experimental kinetic and molecular species data:



where M = a metal atom
x,y,z = number of atoms

It can be postulated that by forming a stable non-mobile complex between sodium and sulphur, the sodium is prevented from (a) diffusing into the coke and (b) catalysing the reaction at active sites.



In the case of sodium added (eg cryolite), this would stop reaction almost entirely as the sodium species reacts preferentially with sulphur to form a stable inactive species instead of oxidation of the sodium species to a catalytically active form. However if the sodium was already distributed throughout the coke material in the oxide form (eg from Na₂CO₃ contaminated cooling water, then only a reduction in activity would be expected (and is observed) as the active catalyst is "poisoned" by the sulphur during the redox cycle.

CONCLUSIONS

The dependence of the sodium sensitivity on the coke nature has been considered as a function of the coke sulphur content. From a bench scale procedure the different sensitivity to sodium attack was established. Thermogravimetric analysis showed this to be due to a change in the reaction mechanism. SIMS element mapping showed that during baking, the sodium was bound to the high sulphur coke grains and prevented from migrating. In the absence of sulphur a more uniform sodium distribution was found. CAEM identified the catalytic species as a metal oxide, promoting reaction through nucleation and edge recession. This catalytic activity was arrested in the presence of sulphur. Finally XPS identified a sodium sulphate species, and when excess sulphur was present a second sulphide species.

It is postulated that the lower sensitivity of high sulphur cokes is due to a binding by sulphur of the sodium species in an inactive form preventing catalysis of the gasification reaction. It is believed that this neutralisation takes place during the baking phase of electrode preparation when the temperature is high enough to allow sodium migration.

With the current trend in coke quality to higher sulphur levels, more pressure is being put on smelters to reduce the quantity of sulphur in anodes, primarily for environmental reasons. Consequently coke producers are increasingly being pressured to desulphurise their coker feedstock. This desulphurised coke is much more sensitive to sodium additions and the excess carbon consumption can increase dramatically if it is used in place of less sodium sensitive cokes where sodium contamination is high. However this coke can be used to make excellent quality anodes if attention is paid to the cleanliness of the recycled butts. An excellent review of butts cleaning systems was written by Robert Tonti⁸.

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