

Ergo Forschungsgesellschaft mbH
Geierstrasse 1
22305 Hamburg

To
Secil – Companhia Geral de Cal e Cimento, SA
Att. Ms. Eng^a Maria João
Apartado 71
2901-864 SETÚBAL

Dear Sr^a. Eng^a Maria João,

Within the frame of the co-incineration tests at Secil Outão Eng^a Maria João from Secil passed to Ergo Portugal a document from SGS Portugal that shows the assessment of an SGS expert (the name and the exact company name was not communicated to Ergo) about the quality of the stack testing measurements based on a visit on site in July 2005 (indicated with SGS Portugal: project Secil 11 – 13/7/05).

Conclusions:

Some of the objections of the SGS expert are qualified (consult paragraph G). After checking the systems this has no relevance on the measured results.

In general the expertise clings too much to the details of the measuring procedures. According to our experience this gives more questions than answers. It was not mentioned that Ergo - regarding to the equipment and the experience of the technicians - is under the permanent observation of the German Authorities especially by round robin tests, inspections of the authorities at the measuring site etc (please consult paragraph H).

Some of our concepts were not realised by understanding.

The assessment of the procedure for the sampling of HF is completely wrong (please consult paragraph K) what can be proved within this letter only by presenting the facts. The expertise gives the impression that Ergo works with procedures that cannot fulfil the requirements. We hope that this completely wrong interpretation was up to now not handled to the Setúbal commission or the public.

For possible future audits it is strongly recommended by Ergo to contact the responsible persons at Ergo Hamburg (Dr. Uwe Düwel, Dr. Klaus Berger) to clear the facts. It is evident, that some of the objections made by SGS could have been avoided by better communication.

Comments in detail:

Our comments are organised in such a way that we made first a copy of the SGS comments in italic followed by the Ergo comments.

A) Emission measurements, general

1. Emission measurements by ERGO

The laboratory performs the prescribed discontinuous emission measurements. The laboratory is accredited according to ISO 17025 for all the samplings that were performed. The sampling location and the sampling points in the stack are according the apposite standards.

Ergo comments:

The Ergo Forschungsgesellschaft mbH is not only accredited for EN ISO/IEC 17025 by the accreditation institute DACH, but as well has a so called notification (indicated as § 26 BISO SchG Laboratory) by the German Authorities. This notification in Germany is necessary to perform stack testing within the frame of the verification of limit values given in the operating permission of the plants. In some parts this notification has more rigorous requirements than the EN ISO/IEC 17025 accreditation.

B) Water vapour content

1.1. Water vapour content

Sampling according to prEN 14790

Deviation from the standard: a non heated probe is used (standard prescribes a heated probe): it is possible that the water condensates in the probe and that the result of the measurement is not correct. Use of a heated probe is highly recommended (normative in the standard).

Ergo comments:

The probe was implemented as a glass tube. This is heated very fast by the flue gas to a temperature of the flue gas of about 120°C. To be sure of this the first sample in a series is always abolished. The low content of acid gases exclude the occurrence of an acid dew point above this temperature, so that it is not necessary to take this into account. The standard covers all kind of stack testing tasks as well those where a heated probe is necessary (e.g. SO₂-concentrations in the range of 5000 mg/m³). (By the way: The fact of condensation of water in the probe does not result inevitably to errors. This is only the case if the probe is bent down so that the resulting droplets can fall back in the stack. The position of our probe therefore is horizontal).

C) Velocity, temperature and pressure

1.2. velocity, temperature and pressure

Measurement by a proper method: grid measurement of velocity is done according the points given in EN 13284-1

Deviation from method: according to EN 13284-1 the number of sample points for a stack of 3 m is 20 (when the middle point is not sampled, the method used by ERGO). The number of sampled points was 16. We estimate that the impact on the accuracy of the measurement was low: the difference of the velocity in the different points was low.

Ergo comments:

The number of sampling points recommended by the EN 13284-1 is in fact 20. But the standard does not refer to the problem that with increasing points the sampling nozzle has to be placed very near to the inner wall of the stack at the first and last points. In this area the release of dust deposits from the stack wall or internals are experienced that can result to uncontrolled interferences. The number of sampling points was therefore adapted to the VDI 4200 that refers to 16 sampling points. The distribution of the flue gas velocity is homogenous so that a difference in the results by application of 16 or 20 points can be excluded.

D) Dust monitoring, rinsing

1.3. dust monitoring

According EN 13284-1

Deviations from standard:

- *the part of the sampling system before the filter (nozzle, part of the filter holder) is not rinsed (has to be done with acetone and H₂O_d) (exception: if there is a lot of dust on the filter the lab rinses the parts with H₂O_d): the impact on the results depends on the concentration of the dust and the physical and chemical properties of the dust and the flue gas.*

Ergo comments:

The investigated plants are equipped with fabric filters so that the dust concentration is very low in the range of 1 mg/m³ and often below the detection limit that is about 0,5 mg/m³. The range of the expected dust concentration was known from previous tests. Rinsing under these conditions led to unrealistic high detection limits because each of the steps – weighing of the filter and treatment of the rinsing solution (incl. evaporating and weighing of the residue) gives one detection limit for each procedure that has to be summed up. That one of the rinsing solution is much higher than those of the filter so that the summed up result in this case does not meet the reality.

E) Dust monitoring, filter drying

- *Before and after the sampling the filters are dried at 150°C: before the sampling a minimum temperature of 180°C has to be applied, after the sampling the minimum temperature has to be 160°C. In this case the impact on the results is nihil since the stack temperature is less than 150°C.*

Ergo comments:

The filters are pre-treated in our laboratory by a temperature of 250°C like it is ascertained in the SOP and not only with 150°C. After sampling the filters are dried 20°C above the flue gas temperature. The standard EN 13284-1 in chapter 9 refers mainly to the necessary procedures for dust samples that show a thermal instability. This is not the case for the investigations on hand.

F) Dust monitoring, nozzle size

- *The nozzle is not conform with the standard: the wall of the nozzle tip is too thick. The individual nozzles are not controlled: the nozzles are produced according the requirements of ERGO and each lot is controlled by a test at random by ERGO to see if these requirements are met. If a lot does not comply with these requirements, it is not accepted. The impact of this non conformity depends on the size of the nozzle used (the impact is larger with small nozzles), the quantity and the characterization of the dust (meanly particle size).*

Ergo comments:

We cannot bring in line these statements with the procedures we practice in the laboratory and in our Quality Assurance System. Maybe this is based on difficulties in communication at the sampling site (high noise level).

We think that the SGS statement refers to the glass probes used by Ergo for the sampling of dioxins/furans, PAH, heavy metals and mercury. Those components are measured only at

very low concentrations (ng/m^3 , $\mu\text{g/m}^3$). Sampling by glass probes is not easy to handle at the sampling site. But we prefer this because glass can be cleaned excellent to avoid contamination. On the other hand it makes the rinsing of the probe easy due to the polished surface: this is important to collect the sample without losses. The nozzle is integrated by our glassblower from always one tube.

Regarding those glass tubes they are specified in the quality of material and the dimensions (inner/outer diameter) by an industrial standard. The compliance of this is controlled by reception inspection. In this respect the statement, that Ergo does not control the diameter of the nozzles, is wrong.

The standard EN 13284-1 gives examples for the construction of the nozzles. The wall of the nozzle tip can be 0,2 mm or 0,4 mm (radius of 0,2 mm). In case of our glass tubes - as breakable material - we meet for practical reasons 0,8 to 1 mm. At low dust concentrations, like they are ascertained at the Secil plant, we are sure that there is no influence on the measurement results.

G) Dust monitoring, gas meters

- *According to the procedure of ERGO the time between two calibrations of the dry gas meters (volume meters) is 1 year (which is a very large period): for two of the 4 meters used the calibration was overdue: last calibration respectively 19/4/04 and 27/4/04, so the meters had to be calibrated about three months ago. The impact on the measurement depends on the drift of the gas meters: EN 13284-1 allows a relative fault of the volume measurement of 2%. It is very difficult to assure this accuracy with such a long period (about 15 months) between two calibrations.*

Ergo comments:

The fact that the gas meters are out of the calibration cycle is known at Ergo Hamburg. The delay was caused by the fact that the calibration reference gas meter in the laboratory (Manufacturer: Brooks Mass flow meter) was out of order and that several trials of the manufacturer for repairing failed and this instrument did not pass several times the external calibration by the German Standardisation Association DKD. The permanent declaration of the manufacturer to solve the problem in a short time and the repeated external calibration, gives a remarkable delay altogether.

We are using this type of gas meters for more than 25 years so that the variation of the calibration factor over the time is well known. Based on this the calibration period was chosen for one year that is as well accepted by the German accreditation institute DACH. For example we found for the same suction unit (gas meter incl. Pressure gauge and thermometer) the variation of the calibration factor like follows: Nov. 2001: 0,931; Feb. 2003: 0,934; Nov. 2003: 0,923 and Nov. 2005: 0,929. The maximum deviation over the time of 5 years is less than 2%. Therefore we felt save to use the gas meter under the above mentioned circumstances 3 month out of the calibration cycle.

H) Dust monitoring, general

It was already mentioned that Ergo has not only the accreditation for EN ISO/IEC 17025 but as well the notification by the German Authorities (Laboratory announced by § 26 Federal Immission Law). Within this frame for the referred laboratories it is mandatory to participate on round-robin tests at the Governmental Institution "Hessisches Landesamt für Umwelt und Geologie" where the authorities operate a test channel with adjustable dust concentrations. Failure of the tests give the loss of the notification. The tests refer to low dust concentration and as well to the content of heavy metals in these dust.

Ergo passed the entire mandatory test in the year's 1994, 2000, 2001 and 2003. During these tests the same equipment was used that was used for the Secil measurements. Therefore we are sure that our reported results are correct.

I) Heavy metals and Hg

1.4. heavy metals and Hg

According to EN 14385 (heavy metals) and EN 13211 (Hg)

Deviations from standard:

- *nozzle: see dust sampling. In this standard the requirements for the nozzle are somewhat less stringent*
- *dry gas meter: see dust sampling*
- *the rinsing procedure deviates from the procedure given in the standard: when $KMnO_4$ is used as absorption solution for Hg (as do ERGO) the absorption bottles have to be rinsed with 3% H_2O_2 or a 10% hydroxylammonium solution. None of these solutions are used. We estimate that the impact of the rinsing procedure on the result is minor.*

Ergo comments:

Regarding the nozzle, please consult paragraph H and F.

Regarding the gas meter, please consult paragraph G.

The statement that Ergo does not use the hydroxylammonium chloride is wrong. A solution of 10% of hydroxylammonium chloride solution is used to rinse the sorption bottles. This is important to solve the deposits of manganese dioxide that are formed during sampling and which can include mercury. This must not be used in excess to maintain the oxidising conditions of the potassium permanganate.

The contrary statement of SGS can explained from our side only by the fact that this step of sample conditioning was not made on the sampling site (risk of contamination) but always in the store where Ergo keep the equipment.

J) HCl

1.5. HCl

According to EN 1911

Deviations from standard:

- *nozzle: see dust sampling. In this standard the requirements for the nozzle are somewhat less stringent*
- *dry gas meter: see dust sampling*

Ergo comments:

Regarding the gas meter, please consult paragraph G.

K) HF

1.6. HF

According to VDI 2470 Blatt 1

Deviations from standard:

- *Absorption solution is H₂O_d. The absorption solution to use, according to the standard, is 0,1 N NaOH. The solubility of HF in H₂O is very low: 0,9 mg/l. The use of H₂O as absorption solution is questionable. Is this procedure validated?*

Ergo comments:

We are sorry, but this assessment is absolute nonsense. The solubility of HF in water is excellent! In contrast to the assumption of the SGS expert the solubility being only 0,0009 g/l (equivalent to 0,9 mg/l) the actual solubility is more than 480 g/l. It is not even necessary to search in scientific tables because the catalogues of the suppliers of laboratory chemicals (e.g. Merck, Sigma-Aldrich) show that HF is sold with a content of 40% to 48% of HF as solution in water.

Of course we validated the procedure with the sorption in water. Comparative tests show that there is no difference to the procedure with NaOH solution. The procedure is described in a Standard Operating Procedure, accepted by the accreditation body and as well accepted by the German Authorities.

L) O₂, CO₂, NO_x, CO and TOC

1.7. O₂, CO₂, NO_x, CO and TOC

According to the following standards: ISO 12619, EN 14792, pr EN 14789

Deviations from standard:

- *Leak check: the check is not performed for the complete system: done for the system without the heated sampling probe. The probe for the sampling of SO₂ is used as probe for both TOC and O₂, CO₂, CO en NO_x measurement (TOC has a separate heated sampling line): therefore it is not sure that there is no leak in the connection of the probe and the two heated sampling lines. The impact on the result depends on the leak in the system, so it is important to perform the leak check for the complete system.*

Ergo comments:

The statement gives the impression that the normal case is to have leakages in the sampling systems. Of course our aim is to avoid leakages already by the concept. Industrial standard glass tubes are used that are identified as not broken and gives no wholes from one day to the other. The flexible hoses from Teflon are checked regularly in the laboratory before this will be used in the field, as well the heated sampling lines. Teflon hoses will be replaced regularly by new ones. The connections are made by grinded spherical ball joints. Within the frame of the calibration of the analysers feeding of nitrogen into the heated line and the filter is done. In case of leakages oxygen can be detected.

In addition of this a permanent leakage control is installed. Two oxygen analysers are used; one of them is equipped with a completely independent sampling system. The correlation of this two independent measured oxygen contents is a strong indication for the lack of leakages.

M) SO₂

1.8. SO₂

According to VDI 2462 and prEN 14791

Deviations from standard: none

Ergo comments:

None

N) Dioxins/ Furans

1.9. Dioxins/furans

According to EN 1948

Deviations from standard:

- nozzle: see dust sampling.
- dry gas meter: see dust sampling

Ergo comments:

Regarding the nozzle, please consult paragraph H and F.

Regarding the gas meter, please consult paragraph G

O) PAH

1.10. PAH

See dioxins/furans: the same sampling procedure is used

Ergo comments:

Regarding the nozzle, please consult paragraph H and F.

Regarding the gas meter, please consult paragraph G

With kind regards

Dr. Uwe Düwel