PUMPS AND MATERIALS FOR FLUE GAS DESULPHURIZATION PLANTS

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ABSTRACT

In the commonly mostly employed, so-called "wet technique" for the desulphurization of flue gas, stringent demands are being made on the materials of the pumps to minimize wear by corrosion and abrasion and to reach the longest possible service lives for the pumps.

For various metallic corrosion resistant materials from several different suppliers, extensive laboratory investigations have been carried out, testing them in a "grinding pot," thereby studying the corrosion and abrasion behavior at different flow velocities. Coated materials and welding materials were also tested; various parts were examined for crevice corrosion.

It can be concluded that only certain duplex materials show a sufficient corrosion resistance, depending on the pH-value and chloride content of the flue gas desulphurization suspension, and on certain alloying elements and the heat treatment the materials received.

A presentation of the design executions for an optimum design of pumps in flue gas desulphurization plants is offered. The principal elements of a centrifugal pump, such as impeller, casing, and shaft sealing with a packed stuffing box and mechanical seal are addressed.

INTRODUCTION

Power stations, industrial plants, motor cars and households produce sulphur dioxide and nitric oxides by combustion of fossil fuels. Among the main polluters of the air are the conventional fuels such as hard and soft coals.

In the Federal Republic of Germany statutory regulations limit the admissible emission values [1], e.g., for sulphur dioxide to a maximum of 400 mg/m^3 for power stations working on a coal basis. To guarantee the adherance to these border values the flue gas must be cleaned in desulphurization plants. Many popular techniques have been developed in Japan or in the United States and have been taken over in license, and have been further adapted by German engineering firms. The currently used techniques can be distinguished as dry techniques, half-dry techniques, and wet techniques.

- *Dry Techniques.*When the dry technique is applied [2[the sulphur dioxides of the flue gas are taken up by an absorption mass, e.g., active coke. The enriched coke is fed in, regenerated in the absorber and fed back into the circuit. The SO_2 gas can then be processed further to liquid SO_2, sulphuric acid, or elementary sulphur.
- *Half-dry Technique.* The main disadvantage of the wet technique lies in the fact that the expense for heating the raw gas is very high. In the so-called "half-dry" technique this disadvantage can be avoided, or respectively reduced by adding a small amount of scrubbing suspension, which must be as highly concentrated as possible, to the hot raw gas flow. The water evaporates and the dry crystallized salts are removed together with flue dust in the succeeding dust filters.
- *Wet Techniques.*Among the wet desulphurization techniques, the lime scrubbing techniques dominate. Such techniques are used in West Germany, and the environmental impact of the final products is minimal. Here the wet desulphurization techniques must be named with their final products [3]—sulphuric dioxide (for the production of

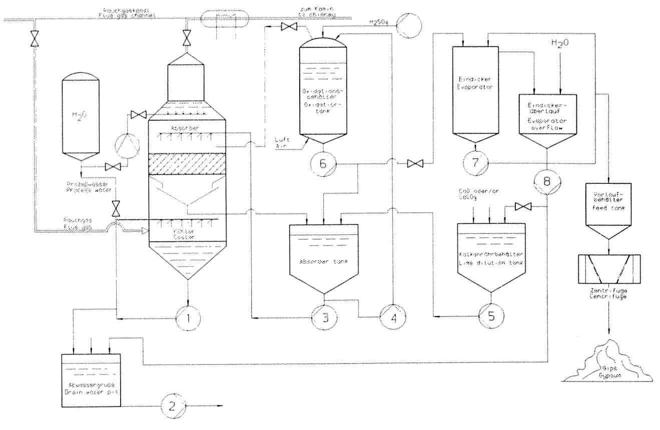

Figure 1. Schematic Sketch of a Flue Gas Desulphurization Plant Using the "Wet Technique" on a Lime Hydroxide or Limestone Basis for the Absorption. Denominatin of the pumps: 1) gas cooling or quench pumps, 2) drain water pit pumps, 3) suspension circulating pumps, 4) slurry pumps, 5) pumps for the absorption solution, 6) pumps at the oxidation tank, 7) evaporator pump, 8) evaporator pump.

sulphuric acid), ammonium sulphate (fertilizer), and calcium, respectively, magnesium sulphite/bisulphite fluid. In the wet technique, mainly calcium hydroxide or limestone is used (Figure 1).

The flue gas is thus purified in the scrubbing towers from the gaseous pollutants, such as

- sulphuric dioxide (SOd2)
- hydrogen chloride (HCl)
- hydrofluoric acid (HF)

The scrubbing suspension consists either of burnt lime [$Ca(OH)_2$] or limestone [$Ca\ CO_3$]. In the absorber circuit the scrubbing suspension is circulated and enriches itself with the reaction products. The concentration of the reaction products is kept on the optimum value by draining part of the fluid and by the addition of fresh scrubbing suspension. In the scrubbing tower, the suspension is sprayed on the flue gases through a system of nozzles. Due to the addition of air, a complete oxidation into calcium sulphate [$Ca\ SO_4$] is achieved. The developing gypsum crystals are removed from the process by subsequent dewatering, i.e., by evaporation. The final product is gypsum [5].

MATERIAL REQUIREMENTS

For pumps used for the most widespread "wet technique with lime hydroxide or limestone," guarantee lives of up to 24,000 operating hours have been demanded.

The application of this process subjects the pump materials to high corrosion and abrasion. With the lime hydroxide absorption medium, the corrosion problems dominate. With the limestone absorption medium beside the corrosion, the abrasion must be taken into consideration, because the air and gas containing suspensions largely consist of chloride and solids (Table 1).

Table 1. Survey on the Composition of Scrubbing Suspensions in Flue Gas Desulphurization Plants.

Operating temperature	normal 40-65°C (104°F-149°F) maximum 70°C (158°F)
pH-value	mostly 4-6 extreme 2-12
Solids content e.g. $Ca\ Co_3$ and $Ca\ SO_4$	minimum 7) percent mostly 10-20) by maximum up to 25) weight
Grain size of the solids	at about 60% up to 50 microns at about 40% up to 200 microns maximum up to 300 microns
Density	minimum 1.02 kg/dm^3 mostly 1.08-1.12 kg/dm^3 maximum 1.2 kg/dm^3
Chloride content	normal 5,000-10,000 ppm maximum up to 30,000 ppm extreme up to 100,000 ppm

MATERIALS

To guarantee a reliable operation and to fulfill the high guarantee and availability requirements, the proper selection of materials is most important. It is even more essential, when a chargefree replacement of the parts by the pump manufacturer is involved, and the guarantee condition of 24,000 hr is not met. The following material groups are applied for pumps today:

- Plastic—Polyethylene
- Metal casing of cast iron, with an inner rubberized coating or mask
- Metal casing of cast iron, with a polyurethane mask and polyurethane cast impeller
- All fluid-touched components in highly alloyed metallic materials.

Neither the highly wear-resistant ferritic-carbide chromium casting types nor the austenitic Cr Ni Mo steel casting types offer acceptable properties for the severe demands due to corrosion and abrasion. Good results are gained with ferritic-austenitic Cr Ni Mo Cu steel casting types with the duplex structure (Table 2).

Table 2. Survey over the Duplex Materials for Pumps in Flue Gas Desulphurization Plants.

DIN material No. 17007 DIN designation 17006		9.4460 G-X 3 Cr Ni Mo Cu 25 6	1.4464 G-X 40 Cr Ni Mo 27 5
Designation U.S.A.		ASTM-A 743 CD 4 MCu	≈ASTM-A 743 Gr.CC 50/ AISI 329
C	%	≤0.04	0.3-0.5
Cr	%	25-27	26-28
Ni	%	5.5-6.5	3.5-6
Mo	%	2-3	2-2.5
Cu	%	up to 3.0	—
Yield stress	N/mm^2	≥450	≥500
Elongation	%	≥25	≥4
Brinell hardness	HB	200-260 solution annealing 300-550 precipitation hardening	250-360

These materials have already been tested with good results in containing fluids sulphate and chloride. They can be used especially for pH-values ≥ 2.5 and offer the highest possible safety against damage caused by pit corrosion, crevice corrosion, intercrystalline corrosion, abrasion, and erosion corrosion.

Duplex materials with copper (Cu content up to about three percent) and nitrogen are, after an appropriate heat treatment, also very resistant against fluids with deep pH-values (≥ 2.5). For suspensions with pH-values ≥ 4, and chloride proportions of a maximum of 30,000 ppm the

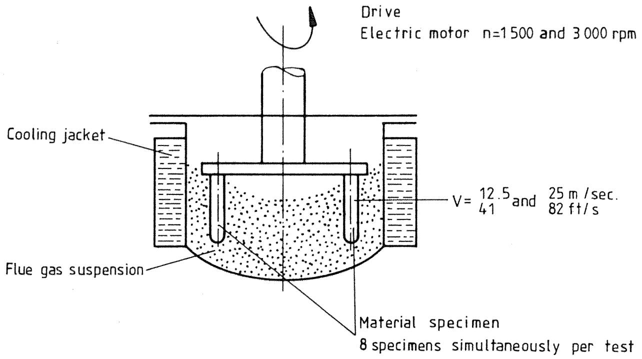

Figure 2. Test Arrangement and Program of the Material Wear Investigations.

Parameter of the scrubbing suspensions:

pH-value	1- 2.5- 4- 6- (10)
Chloride content:	10,000-100,000 (50,000) ppm
Solids concentration:	20 percent by weight and 10 percent by weight with a grain size of 90 microns
Temperature:	about 60°C (140°F)

duplex material without copper, DIN material No. 1.4464 (G-X 40 Cr Ni Mo 25 5) with a Brinell hardness of 250 to 360 may also be employed. To obtain more data for the varying operating conditions on the service life of the applied materials, extensive tests have been carried out in the laboratory. These tests include:

- material wear investigations by corrosion and abrasion.
- crevice corrosion investigations.

MATERIAL WEAR INVESTIGATIONS BY CORROSION AND ABRASION

This study was aimed at identifying corrosion damage at pump parts caused by a too low pH-value of the circuit suspension. The test arrangement and a survey on the test program are depicted in Figure 2.

Besides the most common materials, 9.4460 (with copper) and 1.4464 (without copper), it was also intended to test parts with a wear-resistant surface and a corrosion-resistant hard coating, as well as parts supplied with a hardfacing. The results were to show the repair possibilities with regard to the wear to be expected. Examples of the various specimen materials are given in Table 3.

Table 3. Survey (Excerpt) over the Various Material Specimens.

No.	Chemical composition (%) C	Si	Mn	P	S	Cr	Ni	Mo	Cu	N	Rem.*	Hardness HB
1	.03	.83	.65	.014	.014	24.6	5.44	2.15	2.81	-	L	260
2	the same as No. 1										A	340
3	.03	.78	.83	.011	.009	25.1	5.27	2.09	3.00	.12	L	260
4	.33	1.24	.94	.02	.012	27.3	5.62	2.41	-	-	L	360
5	.03	1.06	1.06	.018	.005	25.0	6.72	3.04	2.66	.189	L	265
6	.03	1.06	1.06	.018	.005	25.0	6.72	3.04	2.66	.189	A	350
7	.04	.69	.75	.021	.010	25.0	6.04	3.18	.99	.157	L	240
8.1	the same as No. 7, detonation coated with LW-5 25 WC + 5 Ni + WCr										B	HCR 69
8.2	the same as No. 7, detonation coated with LW-15 86 WC +10 Co + 4Cr										B	HCR 69
9	.035	1.03	.85	.010	.011	25.4	5.14	2.13	2.99	.14	L	260
10	the same as No. 9										A	325
11A	.015	.85	1.21	.007	.005	22.5	8.73	2.86	-	.14	LS	
11B	.040	.37	.14	.018	.003	20.3	39.4	2.64	1.98	-	LS	
11C	.3	.7	.4			27.6	3.5	6,0	Co:rest		LS	
12A	the same as No. 11 A										AS	
12B	the same as No. 11 B										AS	
12C	the same as No. 11 C										AS	
13	.32	.82	.66	.022	.010	27.2	5.59	2.14	-	-	G	280
14	.03	.88	.38	.019	.007	24.5	5.62	2.12	2.93	.17	L	230
15	.049	.92	.92	.014	.010	21.9	7.20	2.88	1.57	.115	L	215
16	.050	.977	.585	.011	.006	26.0	5.26	2.07	3.10	.155	L	270
17	the same as No. 16										A	355
18	.039	.84	.54	.012	.020	24.5	6.3	2.34	2.91	-	L	260
19	the same as No. 18										A	340
20	the same as No. 14										A	270
21	.025	.050	1.70	.020	.010	27.0	6.50	3.65	2.90	.16	A	550
22	.05	1.11	.56	.19	.012	24.2	6.59	2.75	2.52	.133	L	240
23	the same as No. 22										A	280
24	the same as No. 14										A	340
25	.46	1.18	1.31	-	-	26.3	5.67	2.16	.38	-	E	260
26	.03	.37	.33	-	-	27.4	6.91	3.38	2.72	-	L	290
27	the same as No. 25, detonation coated with LC-1C $80Cr_3C_2$ + 20 Ni-Cr										B	HRC 62
28	the same as No. 25, detonation coated with LW-15 86 WC + 10 Co + 4Cr										B	HRC 69
29	the same as No. 25, plasma coated with LC-4 > 99 % Cr_2O_3										B	HRC 71
30	the same as No. 26, detonation coated with LC-1C $80Cr_3C_2$ + 20 Ni-Cr										B	HRC 62
31	the same as No. 26, detonation coated with LW-15 86 WC + 10 Co + 4Cr										B	HRC 69
32	the same as No. 26, plasma coated with LC-4 > 99 % Cr_2O_3										B	HRC 71
33	1.36	.040	.041	.023	.018	27.7	-	3.13	3.19	.219	W	500
34	.44	.62	.49	.021	.006	26.7	5.42	2.06	2.60	.118	W	285
35	the same as No. 26										A	326

* Remark L: solution annealed, A: hardened, B: coated
S: welded, G: as casting
E: relaxed, W: heat treatment unknown

As a test medium, an artificial flue gas suspension was produced through the addition of sulphuric acid into a limestone powder-water suspension together with NaCl.

Solids content:	20 percent by weight, grain size 90 microns
pH-values:	1- 2.5- 4- 6 and 10
Chloride concentrations:	1 resp. 10%≈10,000 resp. 100,000 ppm (possibly 5%≈50,000 ppm)
Temperature:	about 60°C (±2°C)≈140°F (±3, 6°F)
O_2-proportion:	open system

The production of the media proved to be rather complicated and time-consuming, because the sulphuric acid had to be added drop by drop. The final product was not stable, even after days, when stirred the product and kept reacting in emitting gas and by changing its pH-value. Therefore, the pH-value had to be maintained on the desired value by continually adding HCl, especially in the initial phase of the test. (The addition of H_2SO_4 led to a clogging of the feed pipe by gypsum fallout).

TEST EVALUATION

The average wear rates developed over the trial period (mostly 48 hours) were standardized by referring them to the same area and time and converting them into mm/year. They are depicted in Figure 3 with chloride concentrations of 10,000 ppm and 100,000 ppm.

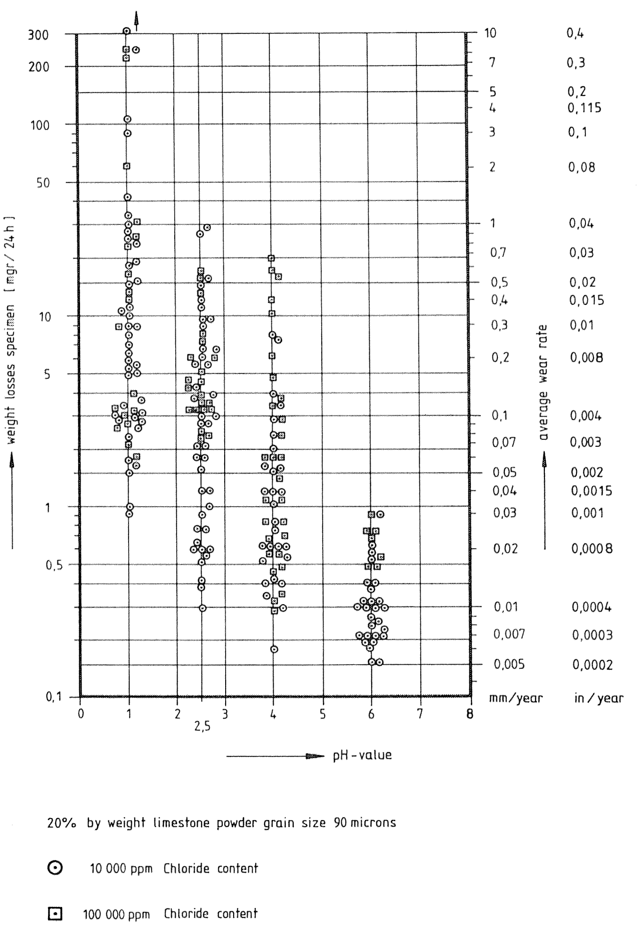

Figure 3. Average Wear Rates of the Various Material Specimens in Function of the pH-value.

The measured results, which were gained at 12.5 m/s and 25 m/s circumferential speed of the specimens are presented in Figure 3. The average values shown must be considered as generally too high in most cases, since the material wear rate was decreasing after some initial time. This was observed in some tests when the same specimens were tested subsequently in 24-hour intervals. This decrease in the wear rate was also backed up by many other tests, in which used material samples were exposed to a futher test.

Possible explanations are:

- greater susceptibility of the surface structure to corrosion after the machining (passive layer also disturbed). After a relatively quick removal of this disturbed passive layer, the behavior of the undisturbed matrix is decisive.

- the relatively great roughness of the freshly machined specimens effects a bigger surface as well as morphology, which suggest greater wear rates by chemical and mechanical impact. After smoothening (polishing effect) of the rough surface exposed initially, the wear rate reaches a smaller value.

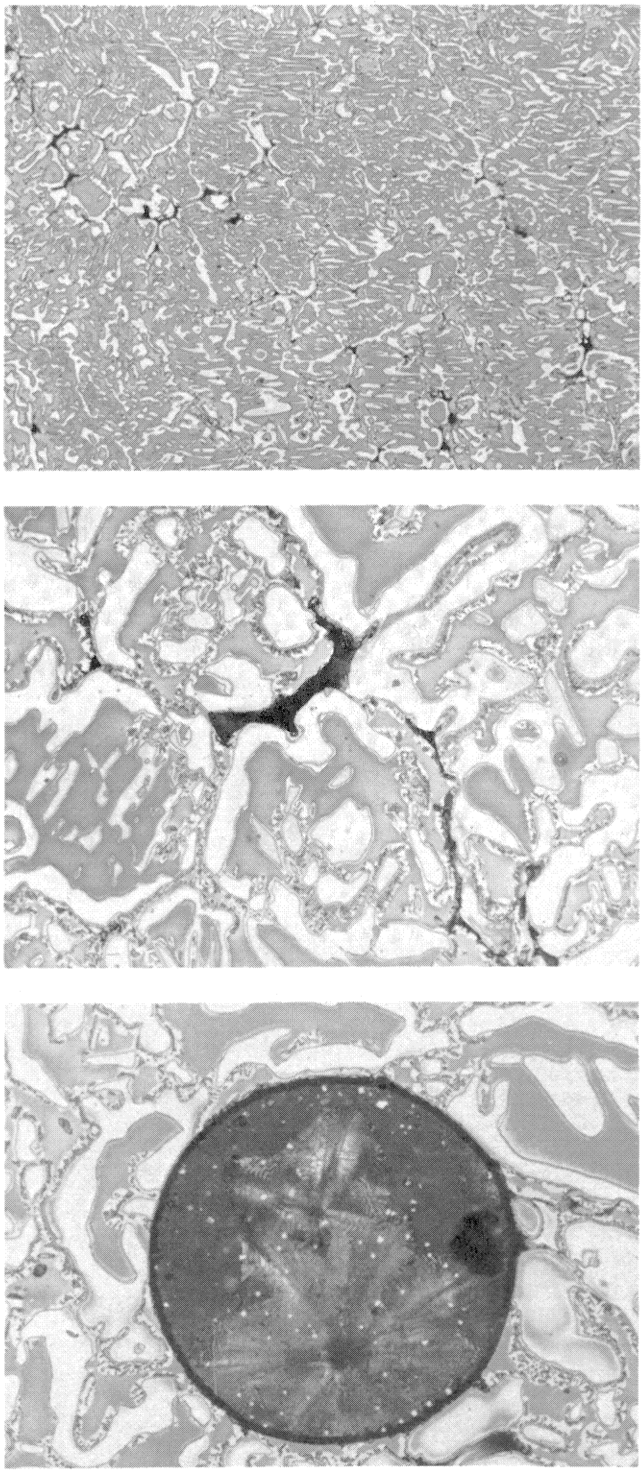

Figure 4. Microstructure of the Material Specimen Number 13 Material 1.4464, Casting Condition, HV about 280. a) Scale 100:1; b) Scale 500:1 c) Scale 500:1.

TEST RESULTS

Generally speaking, it can be stated that there is a large reduction of the wear rate with increasing pH-value. At pH-values over four, the material losses are minimal. At lower pH-values, the difference between the different types of specimens emerges much more distinctly and the variety of the results for a certain material is much bigger. Here, there is a border zone of stability of the passive layer, in which small differences in the medium (pH-value, temperature) or in the material (chemical composition, heat treatment) have relatively strong effects.

The influence of the chloride content must be rated of secondary importance. The general rate of wear is not even affected in a significant way by a tenfold change in chloride content. Alloys which had a relatively bad result at 10,000 ppm frequently had an even worse performance at 100,000 ppm.

Solution annealed and hardened specimens of the same composition show very similar behavior in the results.

The relatively bad performance of specimen number 4 (listed in Table 3) at lower pH-values must be attributed to the lack of Cu and certainly also to the atypical structure, which is probably due to deviations in the heat treatment. The following depictions in Figures 4 through 6 show the material structure of various specimen materials (specimen numbers 13, 21, 26 from Table 3).

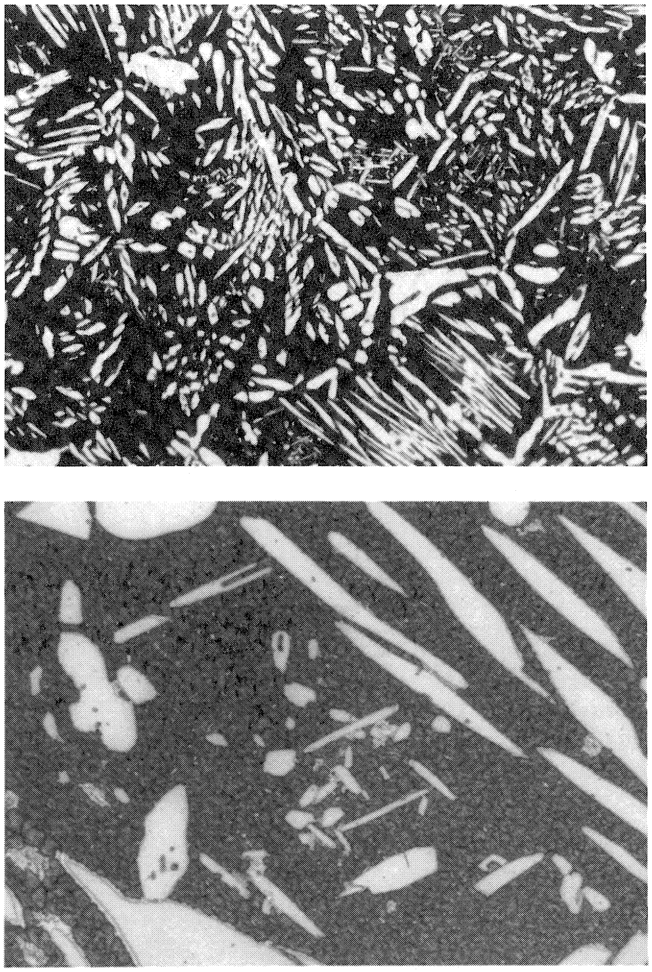

Figure 5. Microstructure of the Material Specimen Number 21 Material 9.4460, Hardened, HB about 550. a) Scale 100:1; b) Scale 500:1.

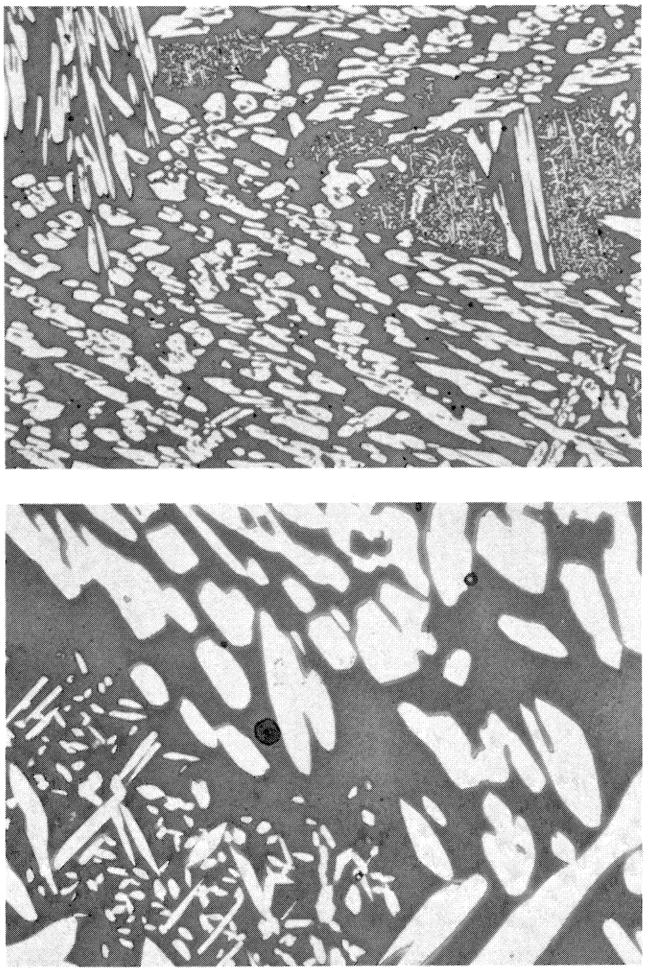

Figure 6. Microstructure of the Material Specimen Number 26 Material 9.4460, Solution Annealed, HB about 290. a) Scale 100:1; b) Scale 500:1.

Material specimen number 13 shows a somewhat unusual phase formation possibly caused by incorrect heat treatment or none at all. At the phase borders, (A/F) sigma and carbide particles can be seen (especially the first ones effect a strong embrittlement as well as a decrease in the corrosion resistance). An unfavorable effect is also to be expected by the big slag inclusions and the large extent of micro shrink holes (Figure 4c).

Material specimen number 21 shows a normal phase distribution (A/F) with the beginning of disintegration of the ferrite in alpha phase and secondary austenite at the phase borders (embrittlement). Granular structure of the ferrite is probably caused by the fine (possibly submicroscopic) separation products of alpha′ and Cu.

Material specimen number 26 shows a normal casting structure with a relatively fine phase distribution and secondary austenite areas.

The specimens with the best performance in the average are marked by higher rates of Mo, Cu, and N. Besides the proportion in special alloy elements, there is also the structure itself, which is very important, i.e., the ferrite content, the type and distribution of inclusions, etc.

CREVICE CORROSION INVESTIGATIONS

In the laboratory, the behavior of the materials 9.4460 and 1.4464 was tested in close to reality crevice conditions, as they arose, for example, during shutdown periods of the pumps without the pumps being drained of the flue gas medium (Figure 7).

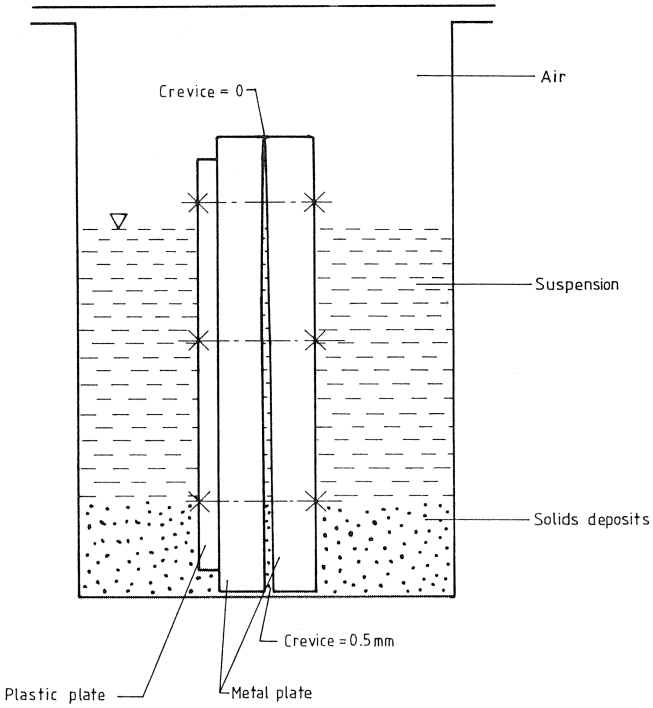

Figure 7. Schematic Arrangement of the Crevice Corrosion Investigations.

Both materials were each exposed to an artificially produced flue gas suspension and to a proper one, taken from an operating flue gas plant.

The following factors are considered the most important values in the analysis of the scrubbing suspensions:

	artificial flue gas suspension "Winterthur"	proper flue gas suspension "plant"
pH-value at 20°C (68°F)	6,9	7,9
Chloride (Cl-) ppm	13.600	6.920
Solids content gr/l	100	80

TEST RESULTS

With the material 1.4464 (without copper), slight traces of corrosion products and also slight corrosion attacks at the edges were found in both suspensions.

With the material 9.4460 (with copper), no attacks or corrosion products whatsoever could be detected under the same conditions. According to this study, pumps with all fluid-touched parts manufactured from materials 9.4460 or equivalent can be applied in flue gas desulphurization plants, without the necessity of a special flushing in case of short blockages. The fluid must adhere to the corresponding conditions (pH-value, chloride content and temperature).

SUMMARY OF THE TEST RESULTS

The results prove that in the case of the employment of suitable metallic materials, e.g., 9.4460 and in a limited way 1.4464 over a pH-value of 2.5, no substantial corrosion or erosion wear arises. With the duplex material the "know-how" of the manufacturer in the heat treatment is, among other things, decisive. The proportion of austenite in the duplex composition ought to be ⩾ 50 percent.

Suitable repairing possiblities, in case of not reaching the guaranteed service life, have been found in the techniques of applying coatings by detonation gun process and welding with well-defined materials. These techniques have been tested under reality-related conditions.

The results obtained of the laboratory investigations were also fully backed up by the results gained in the plants. Several pumps were opened in a flue gas desulphurization plant after 8,000 hr, to check the condition. All pump parts were in excellent condition and showed only slight traces of wear—about 0.2 mm at the stationary and rotating wear ring. The pumps were reassembled and put in operation without any repair work.

DESIGN CHARACTERISTICS OF THE FLUE GAS DESULPHURISATION PUMPS

It is essential to the economical operation of the total plant that the availability and easy maintenance and, therefore, a prompt operation of the pumps is guaranteed. A typical centrifugal pump used in flue gas desulphurization is shown in Figure 8. Important design advantages of the pump are:

- simple assembly and disassembly.
- high operating reliability by easily replaceable wear parts among others also mechanical seals.
- optimal hydraulic for high efficiency.
- low noise level.

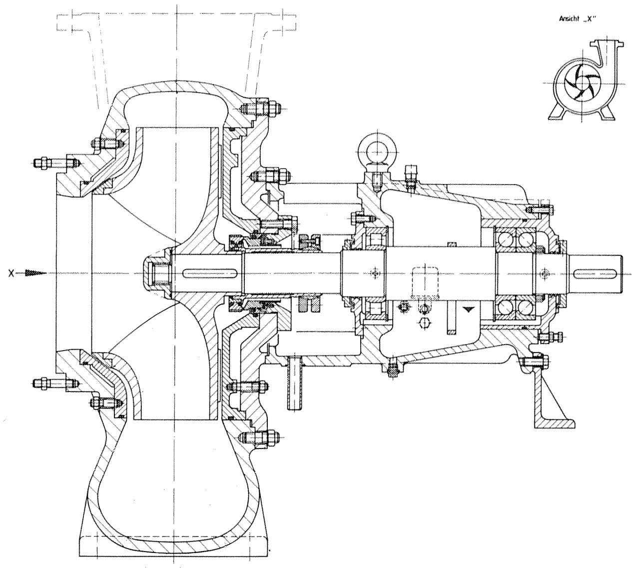

Figure 8. Typical Centrifugal Pump for Flue Gas Desulphurization Plants with Oblique Gap at the Impeller and Single Mechanical Seal.

Application:
For the delivery of limemilk
limestone suspension
filtrate
overflow water
waste water

Operating data: Pump sizes: DN 40 mm-800 mm ≈1½″-32″
Capacities: Q up to 12.000 m^3/h ≈53.000 USgpm
Heads: H up to 80 m ≈267 ft
Operating temperature: t up to 100°C≈212°F
Operating pressures: p up to 16 bar≈232 psi

The types of pumps applied in flue gas desulphurization are single-stage, horizontal volute casing pumps of the process design. This design allows a disassembly of the complete rotor unit with bearing bracket from the driving side. When a coupling with an intermediate piece is used, there is no need to remove the pump casing from the piping system.

The casing is, from the casting point of view, optimized in regard to the use of duplex materials. Replacable wear plates on both sides of the impeller offer an additional protection to the casing. Casing bores for draining, ventilation, etc., are avoided. The shaft is "dry," i.e., it is completely sealed and protected against contact with the fluid. The impeller has an "oblique gap" on the front side in contrast to the usually executed "angular gap."

With this gap form, it is possible to reduce substantially the wear which was caused by the abrupt deviation of the gap flow. The gap on the suction side can be adjusted from the outside by moving the complete rotor. The impeller, designed as a closed channel impeller has, depending on the pump size, up to five Francis type impeller blades, which are specially profiled at the blade entry. By positioning the entrance edge of the impeller blades into the suction mouth, good NPSH-values are achieved and the influence of air in the fluid on the hydraulic characteristics of the pump is minimized.

SHAFT SEALS

The appropriate selection of materials, easy assembly and disassembly, along with the reaching of long service life are deciding factors in the reliability of the pump and, therefore, the efficiency of the plant. The shaft sealing can be affected by either a packed stuffing box or mechanical seal. Both types must be adapted to the corresponding operating conditions.

The simplest shaft seal is a packed stuffing box with flushing ring (Figure 9). Convenient assembly and sealing replacement without disassembly of the pump along with low routine maintenance are the advantages of this type shaft seal. Sealing liquid is put on the flushing ring with about a 1 to 2 bar higher pressure than the pressure to be contained. This prevents the intrusion of fluid under the packing. The biggest part of the flusing liquid rests in a chamber behind the impeller on the discharge side; a small part leaks off. To reach a long service life, the shaft sleeve is manufacture with a "smooth and hard" surface.

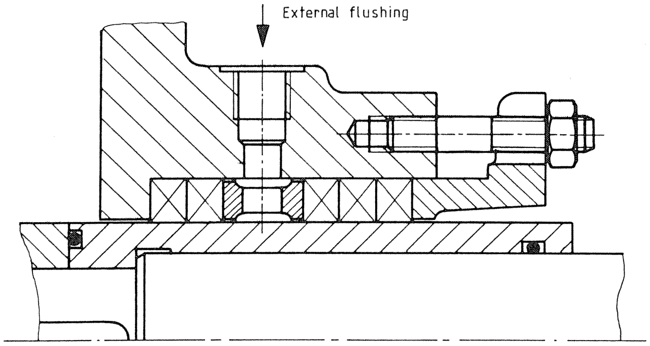

Figure 9. Packed Stuffing Box with External Flushing.

The single mechanical seal (Figure 10) seals off the fluid directly and does not require any flushing with an external medium, when the appropriate choice of materials (e.g., silicon carbide) is made. With the sealing chamber designed open towards the impeller side, a good circulation of the liquid at the sliding surfaces and, therfore, a good removal of the friction heat is ensured. Due to the centrifugal effect of the cone-chaped extension, the heavier particles are held off the sliding surfaces.

The spring is placed outside of the suspension in such a way as to guarantee good operating conditions. With this design, a life expectancy of 16,000 hr for the mechanical seal, even with suspensions previously mentioned, is achieved. The cartridge design allows a quick replacement of the sealing unit in case of a revision.

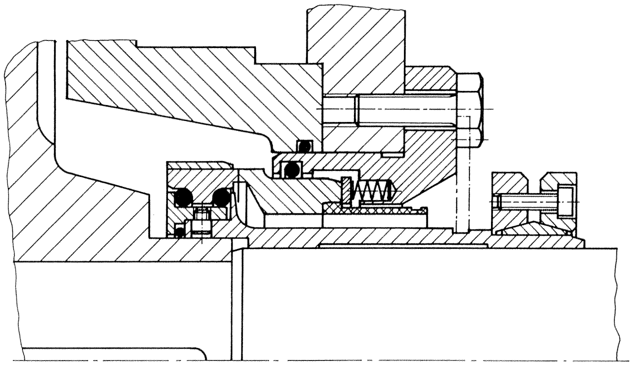

Figure 10. Single Mechanical Seal without Flushing.

When applying a double mechanical seal in back-to-back arrangement an axial fixation, respectively, securing of the product-sided sliding ring must be supplied, to guarantee full availability in case the sealing pressure fails.

CONCLUSION

For today's widespread "wet techniques," stringent demands are being made on the materials of the pumps, due to corrosion and abrasion.

Special duplex materials and heat treatments allow maximum service lives and operating reliability of the pumps.

It has been proved that the studied pumps in flue gas desulphurization plants fully meet the high requirements concerning guarantee and availability, due to good hydraulics and overal optimum design.

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