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HIGH TEMPERATURE MATERIALS FOR RADIOACTIVE WASTE INCINERATION AND VITRIFICATION

by

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ABSTRACT

Incineration or vitrification of radioactive waste subjects equipment to alkaline or acidic fluxing, oxidation, sulfidation, carburization, and thermal shock. It is necessary to select appropriate materials of construction and control operating conditions to avoid rapid equipment failure. Nickel- and cobalt-based alloys with high chromium or aluminum content and aluminum oxide/chromium oxide refractories with high chromium oxide content have provided the best service in pilot scale melter tests. Inconel 690 and Monofrax K-3 are being used for waste vitrification. Haynes 188 and high alumina refractory are undergoing pilot scale tests for incineration equipment.

Laboratory tests indicate that alloys and refractories containing still higher concentrations of chromium or chromium oxide, such as Inconel 671 and Monofrax E, may provide superior resistance to attack in glass melter environments.

INTRODUCTION

Incinerators are being developed to reduce the volume of solid and organic liquid radioactive wastes, reducing the overall cost of storage and disposal. At the same time, incineration converts these wastes to nonflammable ash, and permits the waste to be incorporated into a cement-based form.

Facilities for the conversion of high-level radioactive waste into borosilicate glass are being designed or constructed in the United States, Belgium, the Federal Republic of Germany, Japan, and France. One of these is the Defense Waste Processing Facility (DWPF), described in a companion paper in this volume.[1] The DWPF will process high-level radioactive liquid and sludge wastes from processes at the Department of Energy's Savannah River Plant (SRP).

Laboratory and pilot scale programs have been conducted to evaluate materials for incineration of wastes containing traces of plutonium, and for the vitrification of high-level radioactive wastes. Both types of equipment require operation at temperatures where most alloys and many refractories are rapidly consumed by oxidation, carburization, or fluxing by ash and molten salts. Unlike production processes where corrosive agents can be well characterized, and often controlled, waste disposal processes have limited control over chemical agents fed to the systems and are often subjected to wide fluctuations in chemical species, concentrations, and oxygen fugacities. SRP wastes contain radioactive by-products and large amounts of nonradioactive materials including processing chemicals and soluble salts. Salts contained in the waste which contribute to high temperature corrosion include alkali and alkaline earth nitrates, nitrites, sulfates, chlorides, fluorides, and phosphates. Oxygen fugacity is expected to vary with location in the melter during the combustion of organics used during processing.[2]

High temperature alloys typically rely on the formation of chromia or alumina protective layers which are thermodynamically resistant to the attacking environment, and provide diffusion barriers between the environment and more reactive base metal. Spalling of the protective layers, accumulation of reactive species under the protective layers, or environments thermodynamically favoring the formation of nonprotective layers can lead to rapid failure of such alloys. Although incinerators and melters have similar operating temperatures and corrosive agents in their feeds, differences between oxygen fugacities and the composition of slag or glassy deposits cause major differences in the type of attack which occurs, and the materials which can be used.

Short-term corrosion tests used to select materials of construction for incinerators and waste glass melters at SRP are being compared to longer time performance in pilot scale equipment. Modification of equipment designs or operating conditions may become necessary to lengthen equipment lifetimes.

PLUTONIUM WASTE INCINERATOR CORROSION CONDITIONS

One incinerator under development at SRP is the Plutonium Incinerator (PWI), which will be used to burn solid wastes contaminated with plutonium isotopes 238 and 239. Most of the material burned in the PWI is expected to be paper, chlorinated plastics, and chlorinated/fluorinated/sulfonated rubber gloves containing lead. It is expected that the refractory and a woven metal belt used as a conveyor in the PWI will be exposed to both oxidizing and reducing conditions at 800°C. In addition, carburization can occur by both elemental carbon and carbon monoxide. Alloy embrittlement may be possible from hydrogen, sulfur, oxygen or lead. The atmosphere will contain up to 2500 ppm HCl and 85 ppm NO_x. SO_2 concentrations and the tendency to form sodium sulfate have not been determined.

INCINERATOR TESTS AND DISCUSSION OF RESULTS

Eight alloys were selected with the aid of Shirco, an incinerator manufacturer. The alloys were woven into a herring-bone mesh belt and exposed in a small test incinerator burning nonradioactive, chemically representative waste for 400 hours. The series included highly alloyed stainless steels and iron, nickel, and cobalt base superalloys. The nominal composition of these alloys is shown in Table 1. The four best alloys were chosen on the basis of minimum number of wires thinned or broken during the test, and the amount of reaction of the protective oxide with ash.

Selected for further evaluation were RA 253, AISI 314, Haynes 188, and Inconel 625. In order to evaluate the samples, a random spiral was removed from each belt. Every other diagonal of the spiral supporting the ash was metallographically prepared and measured in cross-section. Fourteen measurements were made on each alloy. The results are shown in Table 2.

Tensile tests were performed at 800°C to simulate the temperature of belt operation. The tests were conducted to determine the alloys with the greatest remaining strength and ductility after exposure to the incinerator environment. Samples were taken from the connector pins, which are the wires immediately below the belt layer contacting the ash. The spiral wire forming the topmost layer of the belt, and most directly in contact with the ash, could not be used for any of the tensile tests because of their shape, and severe embrittlement. Results of the connector pins are shown in Table 3. Six samples of each alloy were tested. The ultimate tensile loads at 800°C were about one half of those of unexposed wires. This was probably due to the reduced area of unaffected metal. Apparently, the reacted layer cannot support tensile stresses.

Embrittlement of all alloys was severe. This may not be a major concern, since the topmost layer of the belt contacting the ash is only subjected to

tensile stresses when it is passed over rollers at either end of the incinerator. It is conceivable that the belt could be broken after it is embrittled by stressing it heavily horizontally, or by dropping a heavy load on it. One measure of embrittlement is the amount of ductility remaining after exposure as compared to unexposed metal. For the four best alloys, percent total elongation to rupture was also measured at 800°C. These data are shown in Table 3. The alloy with the highest total elongation after exposure was Haynes 188. At least part of the embrittlement was caused by an intergranular phase that penetrated to the center of all of the alloys. The intergranular phase was 2-10 microns thick. It was chromium, silicon, sulfur, and chlorine rich in the RA 253, with nickel and iron depletion. Haynes 188 grain boundary layers were enriched in sulfur, nickel, and aluminum, but half-depleted in chromium. There was no evidence of liquid metal attack by the lead.

Based upon these data, a rough estimate can be made of incinerator belt life. A conservative estimate of belt life is a linear extrapolation of the time for conversion to corrosion products because the rate is probably parabolic. Linear extrapolation results in the following approximate lifetimes: Haynes 188 - 3000 hr, Inconel 625 - 2000 hr, RA 253 and AISI 314 - 1000 hr. A thousand hour exposure test is being conducted in a prototype incinerator to verify materials and operating controls.

WASTE GLASS MELTER CORROSION CONDITIONS

Normal melter operating temperatures are 1150°C glass temperature, 600-800°C melter plenum (vapor space) and 950°C for plenum heaters. Plenum heaters are necessary for normal operation to maintain the gas temperature above the auto-ignition temperature of the organics to assure adequate combustion.[2] Under normal operating conditions, one-third to one-half of the halides, nitrates, and sulfates are volatilized and can contribute to

corrosion in the melter vapor space. Alkalis are also volatilized, but not at as high rates. Typical pH is 2.2 for aqueous condensate. Relatively little of the other inorganic waste components are volatilized. However, a small fraction of glass formers and waste components are entrained in the off-gas and can form glassy siliceous deposits mixed or distinct from salt deposits.

WASTE GLASS MELTER EXPERIENCE, TESTS, AND DISCUSSION OF RESULTS

Static and dynamic laboratory coupon tests have been conducted to determine the corrosion rate of alloys and refractories immersed in molten glass.[3-6] See Tables 4 and 5. These tests have sometimes contained sulfates, which have increased the attack of both alloys and refractories.[5] Refractory corrosion rates increase by a factor of 5, and Inconel 690 rates increase by a factor of 3, when the alkali content of high alkali glass is increased from 22.5 to 25 wt % (26 to 33.5 mol %).[5]

Static coupon tests have generally shown that both alloys and refractories partially submerged in glass are most rapidly attacked at the solid/gas/glass interface. This type of attack has not been noted in pilot scale tests, probably because comparable regions in actual melters are much cooler than nominal melter glass temperatures. Extreme wear during actual melter operation is better represented by dynamic corrosion tests, which simulate the convective motion of the glass pool relative to alloy or refractory melter components.[7] High chromium oxide ceramics are more likely to fail by thermal shock (and the dropping out of checked pieces) than by dissolution. As an example, UCAR LT-1 cermet failed pilot scale thermowell testing by thermal shock. Using a composite wall design which limited the temperature gradient across the refractory, cracking and dissolution were not significant after two years of operation, and several more years of operation appear possible.[6]

Glass-immersed coupon tests have generally shown that alloys which form chromium oxide protective layers are more resistant than alloys which form alumina layers. Alloys with exceptionally high chromium contents have shown the greatest resistance to molten glass, with Inconel 690 (30% Cr) the preferred alloy.[6] Generally, the higher the chromia content of a refractory the better its resistance to molten glass,[6] probably the result of lower solubility of chromia in glass and higher resistance to basic fluxing. In molten glasses, the ability of sulfur compounds and halides to flux Cr_2O_3 is limited by glass solution effects which reduce the chemical activity of the corrosive species. The presence of oxidized transition metals in glass keeps local oxygen activities high, suppressing the formation of sulfides, and supporting the development of protective Cr_2O_3 layers. Perhaps one example of the glass solution effect is the difference in composition of salts removed from different locations in a melter. Molten salts removed from the surface of the glass pool were sodium sulfate with 0.25% NaF and 0.03% NaCl. Off-gas line deposits were sodium sulfate with 14% NaF and 9% NaCl.

Most alloys have been unsatisfactory in melter vapor spaces.[8] Inconel 690 is the only alloy tested which has been generally reliable. Alloys having lower chromium content sometimes show satisfactory initial performance, but later suffer from breakaway corrosion and are rapidly consumed.[9]

As an example of melter vapor space corrosion, melter plenum heaters of Inconel 600, 601, and 690 were operated for 20 days at 1000°C. These tests were made in pilot scale melter operations at the Pacific Northwest Laboratory (PNL) using simulated DWPF feed with 0.34% Cl. Melter off-gas contained an average of 100 mg/l SO_2 with a maximum of 800 mg/l SO_2. The 0.2 inch thick plenum heaters were removed at the end of the test and examined visually and by scanning electron microscopy, energy dispersive spectroscopy, and wavelength

dispersive spectroscopy. Inconel 600 had corroded halfway through over its entire surface, with local regions of attack through the entire thickness. The alloy had converted to nickel sulfide, nickel oxide, iron oxide, and chromium sulfide in these regions. Sodium sulfate was present in the porous oxide layers. In Inconel 601, the outer reaction layer was 0.016 inch (0.41 mm) deep, with grain boundary penetration to 0.040 inch (1.02 mm). Inconel 601 corrosion products were chromium sulfide, chromium oxide, and nickel. The Inconel 690 showed no indication of sulfur attack. The measured oxide thickness was 0.0024 inch, but may have originally been thicker and spalled. The exposure time was too short to determine if catastrophic "breakaway" sulfidation would eventually occur.

The high temperature sulfidation resistance of Inconel 690 has generally been adequate. Two year operations with sulfate concentrations at 0.16% of the glass, and halide contents less than 500 ppm of the glass, showed no evidence of Inconel 690 sulfidation.[7]

Recent tests have been conducted with melter feed containing 0.15% sulfate and 0.40% chloride, which is typical of that expected in the DWPF. In one such test, an Inconel 690 thermowell developed multiple pits 40 mils in diameter by 20 mils deep after seven weeks operation. The porous reaction zone had isolated nickel chloride and chromium sulfide inclusions. Based upon current understanding of breakaway corrosion, it is doubtful that the pitting would have proceeded much further.[10] The pits were found under splattered glass layers on a thermowell. It is most likely that molten salt deposits resulted in rapid pitting during initial operation, and subsequent glass splatter stopped the reactions with the alloy. At PNL, the flat top of an Inconel 690 electrode was found to be pitted after six weeks operation with the same melter feed. Maximum pit depth was approximately 40 mils. Approximately one-third

of the grain boundaries in the reaction zone were chromium sulfide, which is closer to achieving breakaway corrosion sulfide morphology.

In only one case has breakaway corrosion of Inconel 690 occurred in a melter. In the PAMELA project melter, the 0.25 inch thick off-gas line was perforated in six weeks operation with melter feed containing 0.5% sulfate, and 1.2% fluoride. It is believed that salts accumulated in the horizontal section of the off-gas pipe during operation with the melter plenum at 350°C. The resulting deposits were about 0.1 inch thick. During subsequent idling, thermal radiation from the molten glass pool melted the deposits, and caused rapid sulfidation of the Inconel 690. The deposits were determined to be mixtures of sodium sulfate, molybdenum, and iron salts. Fluoride was not a major salt constituent, but may have been present at the start of the corrosion. Recurrence is being prevented by plasma coating the inside of the Inconel 690 line with a FeCrAlY sulfidation resistant coating, and by limiting the temperature in this area during melter idling.[11]

In response to the sulfidation at PAMELA, SRL conducted a statistically designed set of coupon tests. The primary objectives of the study were to 1) duplicate the Inconel 690 attack at PAMELA, 2) determine the effect of differences between PAMELA and DWPF melter conditions on sulfidation, and 3) determine if the DWPF is susceptible to a similar problem. Corrosion tests were conducted on 1/8 inch thick Inconel 690 coupons partially submerged in salt mixtures contained in high purity alumina crucibles with lids. Forty-six Inconel 690 coupons were partially submerged in various mixtures of sodium/sulfur salts, redox agents, and reagents simulating deposits found in melters. Five variables were examined, with three test levels for each variable. The test also contained separate control samples heated in air,

or heated in pure sodium sulfate. Variables were as follows:

XI) Oxidation state of Na_2SO_4:
30.00g Na_2SO_4, 26.63g Na_2SO_3, or 50.73g $Na_2S.9H_2O$

X2) Halide content:
3.10g NaF, 1.50g NaF & 2.16g NaCl, or 4.32g NaCl

X3) Oxidation state of molybdenum:
11.23g Na_2MoO_4, blank, or 13.04g $(NH_4)_6Mo_7O_{24}.4H_2O$

X4) Saturation of nickel oxide:
blank, 1.5g NiO, or 3.0g NiO

X5) Alkali fluxing:
5.76g Na_2O_2, 2.954g NaOH, or blank

Reagents were ratioed to sodium sulfate on an equimolar basis, or with ratios similar to those seen in actual deposits (see Table 6). The samples were isothermally treated at 850°C for seven days, broken out of the crucibles, pickeled in 1 M nitric acid, and the % weight-loss calculated. The alumina crucibles were not examined in detail.

Statistical analysis of variance calculations were used to determine which variables were significant at the 95% confidence level. The strongest effect was the oxidation state of the sodium sulfate, with reduced species the most corrosive. Overall conditions in a melter are not expected to get more reducing than Na_2SO_3, but might be more reducing in heavy deposits adjacent to reacting metal, or in the presence of carbonaceous soot. The other significant effect noted was an increase in corrosion rate when going from controls containing no halides to all the other tests, which contained halides. No attempt was made to determine the critical halide content in the salt mixtures, since all the test mixtures had halide concentrations typical of actual salt deposits. There were no statistically significant effects with molybdenum, nickel, and alkali fluxing.

A second series of tests was conducted to determine the temperature effect between 650 and 1150°C. Inconel 690 was rapidly attacked by thick deposits of three different salt mixtures at all temperatures above 650°C.

A third test series compared the relative resistance of high-chromium nickel-base alloys to sulfidation by salts representative of glass melter deposits. This was suggested by comparison of the compositions and conditions of the Inconel 600, 601, and 690 plenum heaters discussed above. Glass immersion tests of refractory indicated that chromium oxide is more beneficial than aluminum oxide in the waste glass melting environment.[6] It has also been shown that aluminum oxide is subject to acid or alkali fluxing over a wide range of redox conditions.[12] It is, therefore, assumed that in a glass melter environment, with entrained glass deposits throughout the melter vapor space, alloys utilizing aluminum oxide protective layers will be less resistant than those utilizing primarily chromium oxide. Four salt mixtures, based on Na_2SO_3 with NaCl, NaF, $(NH_4)_6Mo_7O_{24}.4H_2O$ and NaOH fluxing agents were used to test chromium metal, Inconel 671 and 690, and Allcorr. Chromium was discolored, or developed surface scale, but was substantially unaffected. Inconel 671 was discolored in three cases, and almost completely destroyed in the Na_2SO_3/NaCl/NaF/NaOH mixture. Allcorr was essentially consumed in all except the Mo containing mixture. Inconel 690 was totally consumed in three of the mixtures, and essentially consumed in the mixture containing Mo. These tests may be more severe than actual operations, but their short exposure times relative to actual operating requirements make them satisfactory for scouting tests. The high chromium hypothesis was supported by the results: chromium had the best performance, with Inconel 671 much superior to Inconel 690. Allcorr and Inconel 690 were comparable, indicating that high molybdenum, and exceptionally low iron content in Allcorr were not significant differences in these tests.

Based upon these tests and observation of material responses in pilot scale melters, substitution of higher chromium content nickel base alloys will reduce the risk of sulfidation attack, but will not prevent the attack if heavy molten salt accumulations occur. Higher chromium content alloys can be subject to thermal instability, which can result in loss of strength or ductility, and must be considered.[13]

Present coupon tests are studying the interactions between glass and salt deposits on alloy surfaces. Current melter tests are exposing alloys and Monofrax K-3 refractory to typical DWPF concentrations of organics, mercury, sulfates, and halides. Scale melter tests are testing refractory brick designs which seek to minimize refractory spalling and fracture/dropout by maximizing the keying of refractory blocks. The increased tendency for cracking resulting from the higher temperature gradients through the Monofrax K-3 with this noncomposite wall design will be compared to the earlier melter with composite wall design.[7]

SUMMARY AND CONCLUSIONS

Although similarities exist between incinerator and waste melter conditions, differences in operating temperatures, composition of deposits, and oxygen fugacities lead to different choices of materials in these applications. Incinerator alloys are limited by cycles between carburizing and oxidizing conditions, in the presence of chloride and sulfur dioxide. Melter alloys are limited by molten salt deposits, which can lead to sulfidation. Melter refractories are limited by thermal shock, and to a lesser extent, by alkali fluxing locally increased by glass flow over the refractory.

In a pilot scale incinerator, all alloys tested were severely corroded and embrittled after 400 hours exposure. The best alloy, based upon the least thinning of wires, maximum remaining strength, and ductility at operating

temperature was Haynes 188, a cobalt base superalloy. The next best alloys, which were about equivalent, were Inconel 625 (a nickel base superalloy), and 253 (a highly alloyed steel). While projected belt life is adequate, operating or mechanical design changes which would result in operation of the belt at 600°C would reduce the rate of belt failure. A 1000 hour exposure test is being conducted.

For waste glass melters, high chromium content alloys, and high chromium oxide content refractories are the most resistant materials. Alloys and refractories submerged in glass slowly dissolve by alkaline fluxing. With the exception of alloys containing 30% or more chromium, such as Inconel 690 and 671, all alloys tested failed by rapid oxidation, sulfidation, or breakaway corrosion in melter vapor spaces. Even high chromium content alloys can be rapidly attacked by molten salts which condense from the melter off-gas. Therefore, while substitution of alloys can somewhat extend the life of melters, the useful life of alloy melter parts not submerged in glass can best be maximized by avoiding sulfidation conditions. Sulfidation can be prevented through the use of mechanical and operating features which avoid the accumulation of molten salts, or keep alloys below the critical temperature of about 650°C for nickel base alloys. Entrained glass, which fuses to exposed alloy components in the melter vapor space, may increase alloy equipment life by increasing oxygen activity, and decreasing sulfur and halide activities. Since sulfidation of metallic parts can occur rapidly, and the control of salt accumulation is uncertain, one of the most certain ways of extending melter life is to design melters with a minimum number of nonreplaceable metallic parts.

Recent work in controlling corrosive deposits[14], and soot[15] have not been applied to waste melter design and operations, but may become necessary.

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35 Ni/19 Cr was produced by Carpenter Technology Co.
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TABLE 1

Nominal Compositions of Alloys Tested for Incinerator Belts

Alloy	Content, (Wt.%)							
	Fe	Ni	Cr	Mn	Si	C	Al	Others
Driver Harris 901	67	--	20	0.5	0.3	7	5	--
RA 253	63	12	22	0.8	2	0.1	--	--
AISI 314	50	20	25	2	3	0.2	--	--
35 Ni/19 Cr	43	35	19	--	2	0.2	--	1.2 Nb
Inconel 601	14	60	23	0.5	0.2	0.05	1.4	0.5 Cu
Haynes 188	3	24	24	1.2	0.5	0.2	--	31 Co, 16 W, 0.4 La
Inconel 625	2	62	22	0.2	0.2	0.05	0.2	9 Mo, 3.6 Nb, 0.2 Ti
Driver Harris 245	1	75	20	0.5	1	0.05	3.0	--

TABLE 2

Remaining Metal Diameter - Four Best Incinerator Belt Alloys (inches)

Alloy	Average Diameter	Minimum Diameter	Maximum Diameter
Haynes 188	0.053 ± 0.008	0.037	0.062
Inconel 625	0.048 ± 0.006	0.040	0.058
RA 253	0.037 ± 0.007	0.026	0.051
AISI 314	0.036 ± 0.007	0.028	0.049

TABLE 3

Mechanical Properties of Incinerator Belt Alloys After 400 Hour Exposure (Tensile Tests at 800°C)

Alloy	Ultimate Tensile Load, pounds			Elongation to Failure, %		
	Mean Peak	Minimum	Maximum	Mean	Unexposed	Loss
Haynes 188	139 ± 7	128	148	7.6 ± 2.1	60	87
Inconel 625	103 ± 18	83	138	3.4 ± 0.8	105	97
RA 253	75 ± 10	59	85	5.7 ± 2.0	40	85
AISI 314	65 ± 5	53	73	3.6 ± 1.4	30	87

TABLE 4

Nominal Composition of Alloys Tested for Waste Glass Melters (3-8)

Material	Cr	Ni	Fe	C	Mo	Other
Titanium						
Tantalum						
Platinum						
Molybdenim						
Tin Oxide						
Titanium Diboride						
Chromium						
304L Stainless Steel	20	9	bal	0.03		
310	25	20	bal	0.25		
330	18	35	47			
347	17	9	bal	0.15		
410	12		bal	0.15		
446	25		75			
Inconel 600	15.5	76	8			
601	23	60	14	0.15		1.4 Al
617	22	54			9	1 Al, 12.5 Co
625	21	61	2.5		9	3.7 Nb & Ta
671	48	50				0.35 Ti
690	30	60	10			
Incoloy 801	20	32	44			1.13
802	21	32	46			
Hastelloy C-4	18	bal	3	0.02	17	0.7 Ti, 1 Mn
X	22	bal	18	0.1	9	1 W, 2 Co
Haynes 188	24	24	3	0.2		31 Co, 16 W, 1.2 Mn, 0.4 La
25	21	10	3			54 Co, 15 W
Teledyne Allcorr	31	56			10	2 W, 0.25 Ti, 0.25 Al
UCAR LT-1	77					22 Al_2O_3

TABLE 5

Nominal Composition of Refractories Tested for Waste Melters (4-6)

Refractory	Cr_2O_3	Al_2O_3	SiO_2	ZrO_2	Fe_2O_3	Na_2O	MoO	TiO_2
Ruby	9.5	89.5						
#80 Firebrick		45	52				1.4	1.7
Monofrax A2		98.7						
M		94.5	1.1			3.9		
H		93.9				5.6		
S3		50.1	14.3	34.2		1.1		
E	79.7	4.7	1.3		6.1		8.1	
K3	27.3	60.4	1.8		4.2		8.1	
AC-28	32	65	0.1			0.3	0.6	0.03
SERV	16.6	81.1						
Corhart 1215	93							
1780	93							

TABLE 6

Statistical Experiments of Inconel 690 Corrosion in Mixed Molten Salts

Trial #	X1	X2	X3	X4	X5	% Weight Loss
1	Na_2SO_4	NaF	Na_2MoO_4	2xNiO	Na_2O_2	6.01
2	$Na_2S.9H_2O$	NaCl	Na_2MoO_4	2xNiO	Na_2O_2	96.80
3	$Na_2S.9H_2O$	NaF	$(NH_4)_6Mo_7O_{24}.4H_2O$	2xNiO	Na_2O_2	91.23
4	$Na_2S.9H_2O$	NaF	Na_2MoO_4	--	Na_2O_2	87.69
5	$Na_2S.9H_2O$	NaF	Na_2MoO_4	2xNiO	--	95.86
6	Na_2SO_4	NaCl	$(NH_4)_6Mo_7O_{24}.4H_2O$	2xNiO	Na_2O_2	6.92
7	Na_2SO_4	NaCl	Na_2MoO_4	--	Na_2O_2	100.00
8	Na_2SO_4	NaCl	Na_2MoO_4	2xNiO	--	2.13
9	Na_2SO_4	NaF	$(NH_4)_6Mo_7O_{24}.4H_2O$	--	Na_2O_2	6.70
10	Na_2SO_4	NaF	Na_2MoO_4	--	--	17.03
11	Na_2SO_3	NaCl/NaF	--	NiO	NaOH	99.41
12	Na_2SO_4	NaCl/NaF	--	NiO	NaOH	7.14
13	$Na_2S.9H_2O$	NaCl/NaF	--	NiO	NaOH	100.00
14	Na_2SO_3	NaF	--	NiO	NaOH	94.73
15	Na_2SO_3	NaCl	--	NiO	NaOH	100.00
16	Na_2SO_3	NaCl/NaF	Na_2MoO_4	NiO	NaOH	100.00
17	Na_2SO_3	NaCl/NaF	$(NH_4)_6Mo_7O_{24}.4H_2O$	NiO	NaOH	4.62
18	Na_2SO_3	NaCl/NaF	--	2xNiO	NaOH	100.00
19	Na_2SO_3	NaCl/NaF	--	--	NaOH	100.00
20	Na_2SO_3	NaCl/NaF	--	NiO	Na_2O_2	100.00
21	Na_2SO_3	NaCl/NaF	--	NiO	--	100.00
22	Na_2SO_3	NaCl/NaF	--	NiO	NaOH	100.00
23	Na_2SO_3	NaCl/NaF	--	NiO	NaOH	100.00
24	$Na_2S.9H_2O$	NaCl	$(NH_4)_6Mo_7O_{24}.4H_2O$	--	--	87.11
25	$Na_2S.9H_2O$	NaF	$(NH_4)_6Mo_7O_{24}.4H_2O$	2xNiO	Na_2O_2	92.53
26	Na_2SO_4	NaF	Na_2MoO_4	--	NaOH	44.37
27	$Na_2S.9H_2O$	NaF	Na_2MoO_4	2xNiO	--	98.45
28	Na_2SO_4	NaF	Na_2MoO_4	2xNiO	Na_2O_2	1.72
29	Na_2SO_3	NaCl/NaF	--	NiO	Na_2O_2	8.16
30	Na_2SO_3	NaCl/NaF	--	NiO	NaOH	100.00
31	$Na_2S.9H_2O$	NaCl	Na_2MoO_4	2xNiO	Na_2O_2	85.62
32	Na_2SO_3	NaCl/NaF	Na_2MoO_4	NiO	NaOH	100.00
33	$Na_2S.9H_2O$	NaCl	$(NH_4)_6Mo_7O_{24}.4H_2O$	--	--	100.00
34	Na_2SO_4	NaF	Na_2MoO_4	2xNiO	Na_2O_2	100.00
35	Na_2SO_3	NaCl/NaF	Na_2MoO_4	NiO	NaOH	99.17
36	$Na_2S.9H_2O$	NaCl	$(NH_4)_6Mo_7O_{24}.4H_2O$	--	--	5.17
37	$Na_2S.9H_2O$	NaCl	Na_2MoO_4	2xNiO	Na_2O_2	99.61
38	Na_2SO_4	NaF	Na_2MoO_4	2xNiO	Na_2O_2	1.62
39	Na_2SO_3	NaCl/NaF	Na_2MoO_4	NiO	NaOH	2.08
40	$Na_2S.9H_2O$	NaCl	Na_2MoO_4	2xNiO	Na_2O_2	90.11
41	Na_2SO_4	NaF	Na_2MoO_4	2xNiO	Na_2O_2	2.64
42	Air	--	--	--	--	0.172
43	Na_2SO_4	--	--	--	--	0.419
44	Na_2SO_4	--	--	--	--	0.654
45	Na_2SO_4	--	--	--	--	0.067
46	Na_2SO_4	--	--	--	--	1.04