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(54) Title: PROCESS FOR REMOVING MANGANESE FROM WATER

(57) Abstract: The invention relates to a process for removing manganese from an aqueous liquid comprising treating the aqueous liquid with peracetic acid in order to oxidize soluble Mn(II) present in the aqueous liquid to an insoluble manganese compound and optionally with a coagulant, and separating the formed insoluble manganese compound from the treated aqueous liquid.



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PROCESS FOR REMOVING MANGANESE FROM WATER BY TREATMENT WITH PERACETIC ACID

The present invention relates to a process for removing manganese from an aqueous liquid by treating the aqueous liquid with an oxidant and optionally with a coagulant.

Manganese is a common contaminant in natural water sources where it often occurs in association with other metal contaminants, such as iron, aluminium and/or naturally occurring colored compounds. In Finland, raw water is often colored, as turbid surface water may contain humus as well as iron and manganese. The raw water used by Finnish pulp and paper mills is surface water. Also a remarkable part of the domestic water in Finland is surface water.

The main requirements for water quality concern color or humic substances and iron and manganese concentrations. The adverse effect of soluble manganese in drinking water is related to discoloration. Also the growth of iron and manganese - oxidizing bacteria on water mains can lead to general deterioration of the quality of the water distributed. For these reasons standards have been established for maximum concentrations of soluble manganese in drinking water.

Manganese is conventionally removed from water by following scheme: aeration, coagulation, addition of alkali, clarification and sand filtration.

The removal of manganese usually requires oxidation of manganese (II) to higher oxidation states in which manganese precipitates as a solid compound. The most common oxidation state is (IV), but also exist (III) and an intermediate oxidation state between (III) and (II) can be as oxidation product. The chemical formulas are mainly manganese oxides or oxyhydrates. Several methods and chemicals are available for oxidation. In conventional water treatment, manganese removal is carried out for example by oxidising with chlorine, chlorine dioxide, ozone, hydrogen peroxide or potassium permanganate to form solid manganese compounds, which precipitate out of water. The precipitated, solid compounds are then removed from the solution by filtration. Some of these prior art methods will be discussed below.

DE-A1-2408051 discloses a process for removing manganese from water. According to the process an oxidant and sodium aluminate are added to the water to be purified so as to precipitate manganese(IV)-oxyhydrate which can be separated by filtration. Disclosed oxidants are air and/or potassium permanganate.

DE-B-1517542 discloses a process for removing manganese from water. According to the process a water flow is divided into two parts one of which is oxidized with ozone for oxidizing Mn(II) to Mn(IV). The thus oxidized water flow is combined with the other flow resulting in an oxidation wherein Mn(VII) oxidizes Mn(II) to Mn(IV) which precipitates as manganese(IV)-oxyhydrat which can be separated by filtration.

DE-B-1642479 discloses a process comprising oxidizing raw water containing soluble iron and manganese and adding thereto prior to or after or during the oxidation iron(III)-oxyhydrate and manganese(IV)-oxyhydrat. These added substances catalyze the flocculation process and act as a flocculant. The solid containing iron(III)-oxyhydrate and manganese(IV)-oxyhydrate precipitate obtained in the flocculation is separated by filtration. A portion of the solid filter precipitate or sludge is recirculated. The oxidation can be carried out by using air, ozone, chlorine or potassium permanganate.

WO-A-97/34836 discloses the preparation of a coagulant by subjecting a concentrated aqueous solution of a water treatment chemical containing an iron and/or aluminium compound as the main component and soluble bivalent Mn(II) as an impurity to oxidation by means of an oxidant to convert the soluble Mn(II) to manganese dioxide or permanganate. Disclosed oxidants are ozone, hydrogen peroxide, chlorine, chlorine dioxide, chlorate, permanganate and ferrite. The coagulant can be used for removing manganese from raw water, the manganese being oxidized to manganese dioxide due to the presence of a surplus of oxidant in the coagulant.

JP-2003001272 discloses a process for removing manganese from raw water by adding hydrogen peroxide to the raw water in order to convert soluble manganese to insoluble manganese dioxide and removing the formed manganese dioxide particles by membrane filtration.

Some of the oxidants used in the prior art processes are harmful to the environment (chlorine compounds) or suffer from low efficiency or are expensive (potassium permanganate).

An object of the present invention is to provide a simple and efficient process for removing manganese from raw water or other aqueous liquids by using an oxidant which also acts as a biocide preventing the growth of bacteria on water mains.

According to the present invention there is provided a process for removing manganese from an aqueous liquid comprising treating the aqueous liquid with peracetic acid in order to oxidize soluble Mn(II) present in the aqueous liquid to an insoluble manganese compound and optionally with a coagulant, and separating
5 the formed insoluble manganese compound from the treated raw water.

The soluble Mn(II) present in the aqueous liquid is oxidized to a higher oxidation state in which manganese precipitates as a solid compound. The oxidation state is preferably (IV), but can also be (III) or an intermediate oxidation state between (III) and (II). Also mixtures of insoluble manganese compounds can be formed during
10 the oxidation. Preferred insoluble manganese compounds are manganese oxides and manganese oxyhydrates, and especially preferred are manganese(IV) dioxide and manganese(IV) oxyhydrate.

In one embodiment of the invention the aqueous liquid is treated with a coagulant before the treatment with the peracetic acid. This order of treatment results in
15 good manganese removal. The flocculated substance including organic matter can be removed before the treatment with the peracetic acid.

In another embodiment of the invention the aqueous liquid is treated with a coagulant after the treatment with the peracetic acid.

Good results in respect of manganese removal are obtained when the retention
20 time of the treatment with the peracetic acid is from 1 minute to 24 hours. This applies to both the case where the aqueous liquid is treated with the coagulant before the treatment with the peracetic acid and the case where the aqueous liquid is treated with the coagulant after the treatment with the peracetic acid.

The coagulant can be an inorganic coagulant, preferably an iron or aluminium
25 compound. The iron compound can be a divalent or trivalent iron compound, preferably a trivalent iron compound, such as ferric sulphate or ferric chloride. A preferred aluminium compound is polyaluminiumchloride. Also other aluminium compounds can be used, such as alum (aluminium sulphate).

The precipitated manganese compound can be separated by filtration, such as
30 sand filtration.

The peracetic acid can be equilibrium peracetic acid or distilled peracetic acid.

Equilibrium peracetic acid (ePAA) is an aqueous solution which preferably contains about 10% to 20% by weight peracetic acid, 13% to 16% by weight hydrogen peroxide and 21% to 26 % by weight acetic acid. A typical ePAA contains about 13% by weight peracetic acid, 15% by weight hydrogen peroxide and 22% by weight acetic acid.

Distilled peracetic acid (dPAA) is an aqueous solution which preferably contains about 20% to 60% by weight peracetic acid, 0.5% to 1.5% by weight hydrogen peroxide and 1% to 3% by weight acetic acid. A typical dPAA contains about 40% by weight peracetic acid, 1% by weight hydrogen peroxide and 2% by weight acetic acid.

The process of the present invention can be carried out at a pH between 5 and 11, preferably between 7 and 9.

In the embodiment of the invention where the coagulation is carried out before the peracetic acid treatment, the pH of the aqueous liquid after coagulation and before the addition of peracetic acid can be adjusted to 7 or higher, preferably to 8 or higher. The pH after the addition of peracetic acid can be kept at 7 or higher, preferably at 8 or higher. Any suitable alkali can be used for the pH adjustment.

Correspondingly, in the embodiment of the invention where the coagulation is carried out after the peracetic acid treatment, the pH of the aqueous liquid before or during peracetic acid treatment can be adjusted to 7 or higher, preferably to 8 or higher. During the subsequent coagulation the pH is lower.

The peracetic acid is preferably added in an amount of from 0.1 mg/l to 100 mg/l, more preferably from 1 mg to 10 mg/l. The amount refers to the weight of peracetic acid.

The aqueous liquid is preferably raw water including surface water and ground water to be used after the removal of manganese as domestic water including drinking water or as process water for e.g. pulp and paper industry. The maximum concentration of manganese in the raw water to be purified according to the present invention is typically 1 mg/l. The aqueous liquid can also be industrial waste or recirculation water, for example from metal industry or textile industry, or municipal waste water.

In the following the invention will be illustrated by means of examples.

Example 1

The effect of oxidizing agents on the removal of manganese was tested. Tests were done in 1 l batches with miniflocculator. Mn was added to the water to achieve 0.15 mg/l level. The water was coagulated either with polyaluminium-chloride (PAX-18) or with ferric sulphate (PIX-322). Oxidants were added before or after the coagulant. The Mn concentration was analysed from the water after filtration. pHs of the tests were between 4.4-5.0 when ferric sulphate was used as coagulant and between 5.6-6.2 when polyaluminiumchloride was the coagulant. Detailed description of the test procedure is listed below.

10 The coagulation procedure when the oxidant was added before the coagulant was as follows:

- Rapid mixing: 400 rpm, 30 s
- 1st rapid mixing → oxidant addition
- 2nd rapid mixing → pH adjustment so that after the addition of coagulant the pH is about 6.0, when polyaluminiumchloride (PAX-18) was used as coagulant, and about 4.5, when ferric sulphate (PIX-322) was used as coagulant
- 15 3rd rapid mixing → coagulant addition
- Slow mixing: 30 rpm, 30 min
- Sedimentation 30 min
- 20 ■ Filtration

The coagulation procedure when the oxidant was added after the coagulant was as follows:

- Rapid mixing: 400 rpm, 30 s
- 1st rapid mixing → pH adjustment so that after the addition of coagulant the pH is about 6.0, when polyaluminiumchloride (PAX-18) was used as coagulant, and about 4.5, when ferric sulphate (PIX-322) was used as coagulant
- 25 2nd rapid mixing → coagulant addition
- Slow mixing: 30 rpm, 30 min
- Sedimentation 30 min
- 30 ■ Decantation (500 ml)
- Oxidant addition to the supernatant
- Sedimentation 15 min
- Filtration

The results of the experiments are shown in Table I. 5 min delay time at high pH before the coagulant addition is used in one test point (dPAA*).

5 ePAA = equilibrium peracetic acid (aqueous solution containing about 13% by weight peracetic acid, 22% by weight acetic acid and 15% by weight hydrogen peroxide)

dPAA = distilled peracetic acid (aqueous solution containing about 40% by weight peracetic acid, 1% by weight hydrogen peroxide and 2% by weight acetic acid)

NaClO = sodium hypochlorite (as a reference)

10 **Table I** Effect of oxidant (ePAA, dPAA, and NaClO) on manganese removal. Ferric sulphate (PIX-322) and polyaluminumchloride (PAX-18) coagulants were used in the tests. Oxidant was added before or after the coagulation. "pH after 5 min" refers to coagulation pH registered 5 min after the beginning of slow mixing. The dose of ePAA or dPAA is calculated on the basis of active substance i.e. as
15 100% PAA.

	Oxidant	Dose	pH	Mn
		ppm	after 5 min	mg/l
Initial +Mn	-	-	6.4	0.150
PIX-322 (ferric sulphate) 50 mg/l	-	-	4.5	0.094
Coagulant after oxidant	ePAA	2	4.4	0.075
	ePAA	8	4.5	0.087
	dPAA	2.3	4.8	0.076
	dPAA	8	4.8	0.075
	dPAA*	2.3	4.4	0.032
Coagulant before oxidant	ePAA	2	4.5	0.039
	ePAA	8	4.4	0.043
	dPAA	2.3	4.5	0.042
	dPAA	8	4.4	0.043
Initial +Mn			6.7	0.150
PAX-18 (polyaluminumchloride) 30.7 mg/l	-	-	6.0	0.095
Coagulant after oxidant	ePAA	2	6.1	0.110
	ePAA	8	5.9	0.110
	dPAA	2.3	5.6	0.095
	dPAA	8	5.8	0.010
	NaClO	2	5.8	0.095
	NaClO	8	6.0	0.092
Coagulant before oxidant	ePAA	2	6.2	0.080
	ePAA	8	6.2	0.081
	dPAA	2.3	6.0	0.080
	dPAA	8	6.1	0.049
	NaClO	2	6.1	0.081
	NaClO	8	6.0	0.077

* 5 min delay time before the coagulant was added

Initial manganese concentration of the tested water was 0.15 mg/l. After coagulation the concentration was 0.094 mg/l or 0.095 mg/l. Both ePAA and dPAA were able to oxidize some of manganese when ferric sulphate was the coagulant. Both addition points also worked. Better results were achieved if ePAA/dPAA was added after the coagulation with ferric sulphate. Apparently more oxidant is consumed by other compounds if the oxidant is added before the coagulant. This leads to lower removal degree of manganese. Another explanation may be that residual iron accelerates the oxidation of manganese by per-products. Obviously, also the precipitation of the organic matrix "releases" Mn so as to be easier to be oxidized.

5 min delay time before ferric sulphate addition increased considerably the reduction of manganese. This is owing to longer oxidation time at higher pH.

- ePAA was not able to oxidize manganese, when the coagulant (polyaluminium-chloride) was added after oxidant. A higher dose of dPAA was very effective in removing manganese if the addition point was before coagulant. NaClO, if added before coagulant, was not able to remove manganese. If ePAA was added after coagulation with polyaluminumchloride it was able to remove manganese. A higher dose of dPAA was more effective also in this case. NaClO was as effective as ePAA in this case.

10 Example 2

The effect of oxidants on manganese removal is shown in Table II. In these tests the oxidant is added straight to the water. pH was adjusted to 8.5 with 0.1-M NaOH in tests 2-5. Oxidant was added after the pH adjustment in these tests. KMnO_4 was used in test No. 5 (as a reference).

- 15 **Table II** Effect of oxidants (dPAA and KMnO_4) on manganese removal. pH was adjusted to 8.5 with 0.1-M NaOH in the tests 2-5. Oxidant was added after pH adjustment. The dose of dPAA is calculated on the basis of active substance i.e. as 100% PAA.

Test	KMnO_4 ppm	dPAA ppm	pH 3 min	pH 10 min	pH 30 min	Mn, mg/l 10min	Mn, mg/l 30 20 min
1	-	-	5.9	-	-	0.28	-
2	-	5	7.0	6.9	6.9	<0.02	<0.02
3	-	1	7.8	7.6	7.4	<0.025	<0.025
4	-	0.5	8.0	7.7	7.5	<0.05	<0.05
5	0.6	-	8.2	8.1	-	0.02	-

- Initial Mn concentration in 0-test (test 1) was 0.28 mg/l. dPAA oxidized manganese very effectively at high pH. KMnO_4 was also able to oxidize manganese.

Example 3

3.1 Raw water properties

Water sample was surface water taken from a river in western Finland. Because manganese content was enough high for detecting effect of different treatments it

was not needed to add any extra manganese. The composition of the water sample is set forth in Table III.

Table III

pH		6.2
Mn	mg/l	0.356
Fe	mg/l	0.321
Permanganate value	mg/l	77
Conductivity	$\mu\text{S/cm}$	221
Turbidity	NTU	8.6
COD _{Cr}	mg/l	20
TOC	mg/l	15

- 5 The influence of pH on Mn content was studied by changing pH to more acidic and more alkaline direction. The results of the experiments are shown in Table IV.

Table IV

pH	Mn
	mg/l
4.1	0.353
4.8	0.353
6.2	0.352
7.1	0.331
7.5	0.307
8.0	0.297
8.6	0.287
8.9	0.264

- 10 Only a small decrease in Mn content can be detected. At weakly alkaline pH the Mn content was decreased to just below 0.30 mg/l.

3.2 Influence of pH on Mn content at various PAA dosages

The influence of pH on Mn content was studied at various PAA dosages. The results are shown in Tables V-VII. The dosages of dPAA relate to the weight of the PAA solution (the weight of the active substance can be calculated by multiplying the value by 0.4)

Table V

dPAA	pH	Redox	Mn
ppm	end	mV	mg/l
0	6.3	319	0.354
1	6.3	414	0.338
10	6.1	450	0.335
100	5.2	610	0.337

The results in Table V show that if PAA was added without any pH control to water, the Mn content was not changed at all.

Table VI

dPAA	pH	Redox	Mn
ppm	end	mV	mg/l
0	8.1	193	0.309
1	7.6	465	0.325
10	6.9	595	0.290
100	6.1	610	0.237

Table VII

dPAA	Mn, mg/l	
ppm	pH 8.5	pH 9.5
0	0.276	0.188
1	0.258	0.190
10	0.257	0.216
50	0.235	0.205

The results in Table VI and VII show when pH was adjusted to 8 or higher before the addition of PAA, some decreasing in Mn content can be detected. The Mn level remains anyway rather high, too high for industrial usage or household tapwater.

3.3 Effect of iron coagulation on Mn content

In a raw water treatment process the first phase is usually chemical precipitation with an inorganic coagulant. In the experiments ferric sulphate, trade name PIX 322, was chosen as the coagulant. After precipitation and separation of the precipitate, pH was adjusted to desired value, and thereafter PAA was dosed at various amounts with or without additional pH adjustment. The results are shown in Tables VIII-X. The dosages of dPAA relate to the weight of the PAA solution (the weight of the active substance can be calculated by multiplying the value by 0.40).

Table VIII

dPAA	pH	Redox	Mn
ppm	end	mV	mg/l
0	8.1	210	0.353
1	7.0	430	0.277
10	6.7	427	0.014
100	5.6	640	0.126

The results in Table VIII (PIX dosage was 75 mg/l) show that end-pH is affected by the dosed PAA amount. A clear reduction in the Mn content can be seen at dosage 10 ppm at pH 6.7.

Table IX

dPAA, ppm	pH end		Redox mV		Mn, mg/l	
	PIX 322, mg/l		PIX 322, mg/l		PIX 322, mg/l	
	75	150	75	150	75	150
0	8.6	8.6	160	160	0.305	0.217
1	8.5	8.6	255	240	0.137	0.052
10	8.6	8.6	305	355	0.011	0.029
50	8.5	8.5	460	460	0.008	0.005

The results in Table IX show that if pH was kept at a constant value, 8.5 – 8.6, during the whole oxidation period, the Mn content was reduced significantly. A comparison of iron-coagulant amounts of 75 and 150 mg/l showed that a bigger coagulant dosage helps PAA to decrease Mn content.

For studying more detailed the pH effect, the pH was adjusted after coagulation to different levels. The used amount of coagulant PIX 322 was 75 mg/l. The results are shown in Table X.

Table X

dPAA ppm	Mn content at different pH, mg/l								
	5.6	6	6.5	6.7	7	7.3	7.5	8	8.5
1		0.32	0.299		0.277	0.184			0.137
5		0.31	0.163		0.015		0.016	0.016	0.017
10		0.178	0.031	0.014		0.012			0.011
50		0.019	0.016			0			0.008
100	0.126								

5

The results are also shown graphically in enclosed Fig. 1. The results indicate clearly that the lower pH the lesser reduction of Mn content.

Example 4

Additional experiments were carried out as described in Example 3 for another raw water having the composition set forth in Table XI.

10

Table XI

pH		5.2
Mn	mg/l	0.507
Fe	mg/l	0.360
Permanganate	mg/l	14
value		
Conductivity	μS/cm	186
Turbidity	NTU	1.23
COD _{Cr}	mg/l	17

4.1 Effect of iron coagulation on Mn content

The experiments were carried out as described under point 3.3 above. Ferric sulphate (PIX 322) was used as the coagulant. The results are shown in Tables XII- XIV.

15

Table XII

dPAA ppm	pH	Redox mV	Mn mg/l
0	8.5	215	0.473
1	7.1	414	0.409
5	6.9	460	0.096
10	6.1	570	0.008
1	8.6	210	0.248
5	8.5	260	0.005
10	8.5	420	0.011

PIX 322, 20 mg/l

- The results in Table XII show that the end-pH is affected by the dosed PAA amount and that if the pH is kept at a constant value, 8.5-8.6, during the whole oxidation period, the Mn content was reduced significantly. A clear reduction in the Mn content can be seen at dosage 5 ppm.

Table XIII

Fe mg/l	ePAA ppm	pH end	Redox mV	Mn mg/l
10	0	8.5		0.218
10	30	8.4	240	0.055
10	50	8.5	240	0.098
10	100	8.3	240	0.089

Table XIV

Fe mg/l	ePAA ppm	pH end	Redox mV	Mn mg/l
20	0	8.5		0.129
20	10	8.3	300	0.022
20	20	8.4	290	0.021
20	30	8.3	290	0.029

10

The results in Tables XIII and XIV show that also ePAA is effective in Mn reduction and that if the pH was kept at a constant value of about 8.5 during the whole oxidation time, the Mn content was reduced significantly at rather low iron-coagulant dosages.

15

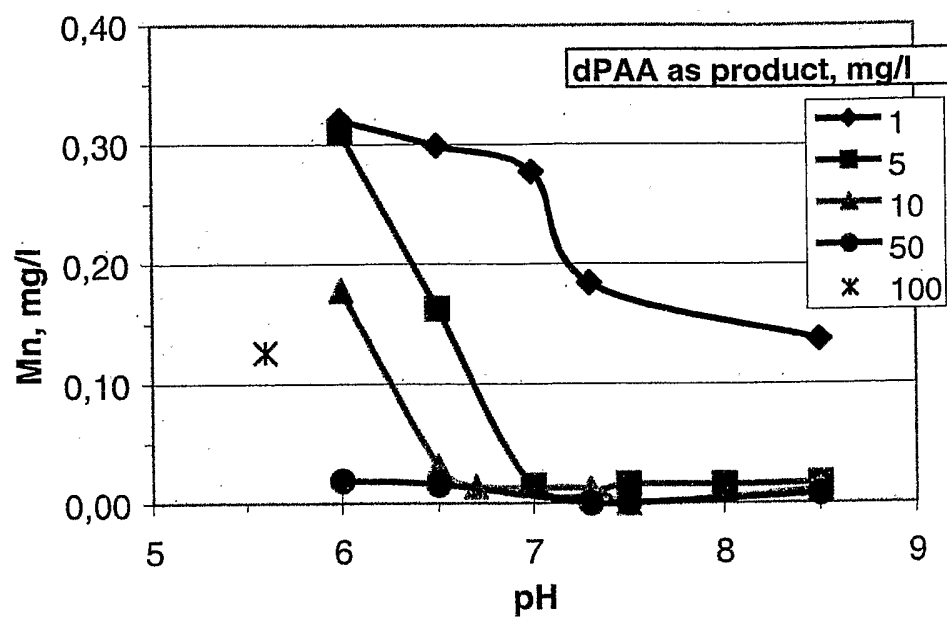
Claims

1. A process for removing manganese from an aqueous liquid comprising treating the aqueous liquid with peracetic acid in order to oxidize soluble Mn(II) present in the aqueous liquid to an insoluble manganese compound and optionally
5 with a coagulant, and separating the formed insoluble manganese compound from the treated aqueous liquid.
2. The process according to claim 1, wherein the aqueous liquid is treated with a coagulant before the treatment with the peracetic acid.
3. The process according to claim 2, wherein the coagulated substance is
10 removed before the treatment with the peracetic acid.
4. The process according to claim 1, wherein the aqueous liquid is treated with a coagulant after the treatment with the peracetic acid.
5. The process according to any of claims 1 to 4, wherein the retention time of the treatment with the peracetic acid is from 1 minute to 24 hours.
- 15 6. The process according to any of claims 1 to 5, wherein the coagulant is an inorganic coagulant, preferably an iron or aluminium compound.
7. The process according to any of claims 1 to 6, wherein the coagulant is polyaluminiumchloride or a trivalent iron compound, such as ferric sulphate.
8. The process according to any of claims 1 to 7, wherein the insoluble
20 manganese compound separated by filtration, such as sand filtration.
9. The process according to any of claims 1 to 8, wherein the peracetic acid is equilibrium peracetic acid or distilled peracetic acid, preferably distilled peracetic acid.
10. The process according to any of claims 1 to 9, wherein the pH is between 5
25 and 11, preferably between 7 and 9 during the process.
11. The process according to any of claims 1 to 10, wherein the pH of the aqueous liquid after coagulation and before the addition of peracetic acid is adjusted to 7 or higher, preferably to 8 or higher.
12. The process according to claim 11, wherein the pH after the addition of
30 peracetic acid is kept at 7 or higher, preferably at 8 or higher.

13. The process according to any of claims 1 to 12, wherein the peracetic acid is added in an amount of from 0.1 mg/l to 100 mg/l, preferably from 1 mg/l to 10 mg/l.

14. The process according to any of claims 1 to 13, wherein the aqueous liquid is raw water including surface water and ground water or the aqueous liquid is waste
5 water.

1/1

**Fig. 1**

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2005/000532

A. CLASSIFICATION OF SUBJECT MATTER
C22B47/00 C22B3/44 C02F1/52 C02F1/64 C02F1/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22B C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 05, 12 May 2003 (2003-05-12) & JP 2003 001272 A (MAEZAWA IND INC), 7 January 2003 (2003-01-07) cited in the application abstract	1-14
Y	DE 24 08 051 A1 (KRONOS TITAN-GESELLSCHAFT MBH) 21 August 1975 (1975-08-21) cited in the application page 1, line 25 - page 2, line 18; claim 1; example 1 ----- -/--	1-14

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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