



COMPATIBILITY BETWEEN ALUMINIUM ALLOY CYLINDERS AND HALOGENATED GASES

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Amendments to 161/16

Title	Change title from “Gas compatibility with aluminium alloy cylinders” to “Compatibility between aluminium alloy cylinders and halogenated gases” to better reflect the content of the document.
3.2	Updating and addition of some definitions
8	Recommendations for tests for new and higher concentration mixtures have been completed.
9	Former section 9 Gas and concentration has been deleted as its content is the scope of the document
10	The description of the method to minimise cylinder moisture content has been removed as it is not specific to the scope of this document.
13	Changed the title of the section from “Results of the analysis” to “Instability of production mixture”.
16	First paragraph has been rewritten for better clarity.

NOTE Technical changes from the previous edition are underlined

1 Introduction

Information on gas material compatibility is given in ISO 11114-1 *Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 1: Metallic materials* [1]¹.

ISO 11114-1 covers the compatibility between pure gases and some common metals and gives some guidance for the compatibility of mixtures with these metals. For mixtures containing halogenated components, the standard gives an overall limit of 0.1% (mol/mol) to be compatible with aluminium alloys. The current experience from the special gases industry is that the limit of 0.1% (mol/mol) may be exceeded provided that the dryness of the gas and of the cylinder is strictly controlled.

2 Scope and purpose

2.1 Scope

This publication details the criteria necessary to establish the compatibility between aluminium alloy cylinders and gas mixtures exceeding the overall limit of 0.1% (mol/mol) reactive halogenated components. The scope of the publication includes fully vaporised liquid components present in gaseous mixtures but excludes liquid mixtures.

The publication does not cover issues relating to the compatibility of valves, valve seat materials or cylinder materials other than aluminium alloy.

2.2 Purpose

The purpose of the publication is to establish rules and criteria to ensure the safe production and use of gas mixtures containing reactive halogenated components that are listed in ISO 11114-1 as incompatible with aluminium cylinders. [1]

3 Definitions

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

3.2 Technical definitions

3.2.1 Cylinder

Transportable receptacle that can be filled with gas under pressure. It excludes small non-refillable cylinders.

3.2.2 Inert gas

Gas that has no other hazard classification than being under pressure.

3.2.3 Internal treatment

Treatment performed on the internal surface of the cylinder.

3.2.4 Reactive gas mixture

Gas mixture that contains halogenated components that can react with the aluminum alloy, which has a detrimental effect on the cylinder structure.

3.2.5 Reactive halogenated component

Component listed in ISO 11114-1 as not compatible with aluminium alloy. See Appendix A. [1]

4 Organization principles

All technical personnel involved in feasibility studies and the calculation and preparation of reactive halogenated components in aluminum alloy cylinders shall be trained, assessed and formally appointed for this activity.

All manufacturing sites filling reactive halogenated components into aluminum cylinders shall be formally qualified by the technically competent company authority for this activity. Qualification shall be based on:

- internal audit programmes;
- the appointment of technically competent qualified personnel; and
- documented procedures and training records.

The company shall define the content of the training and shall define the minimum re-training and assessment periods.

The work instructions shall be version controlled and available at the point of use in the work area.

The organization shall record all of the information necessary to have complete traceability of the preparation and production of such mixtures.

The audit of the preparation and production processes involved in the manufacture of mixtures containing reactive halogenated components in aluminum cylinders should be conducted periodically by a technically competent person. The company shall establish and define this period. For an example of a specimen audit check list see Section 19.

5 Composition of different aluminium alloys and specification

This publication covers any aluminium alloy included in ISO 7866, '*Gas cylinders – Refillable seamless aluminium alloy gas cylinders – Design, construction and testing* [2]. Before considering the use of aluminium alloy cylinders in reactive gas service check internal gas company rules and EIGA safety alerts.

6 Feasibility

The feasibility of producing a mixture containing reactive gases in an aluminium alloy cylinder shall be based on experimental tests, literature studies or other controls, such as establishing the dryness of the gaseous components and the absence of dangerous contaminants in the cylinders.

It should be noted that the compatibility between gases and aluminium cylinders can be modified if impurities are present on the aluminium surface. Special care shall be taken to establish if the presence of impurities change the cylinder compatibility and mechanical properties.

It is recommended that gas companies have specifications for the cylinders suppliers to meet and procedures to control the internal cleanliness of the cylinders received from the manufacturers.

These evaluations shall include an appraisal of safety over the service life of the cylinder, which is the period between cylinder testing.

Before beginning mixture preparation:

- Check if the procedures permit the inclusion of the component at the required concentration or fraction;
- Establish the preparation procedures and any particular precautions required;
- Establish the specification of the gases, with special regard to the impurities than can impact on the compatibility of the mixtures with the cylinder aluminium alloy; and
- Establish the cylinder checks to be performed

It is recommended that cylinders are dedicated to service with a particular component, or at the least chemically similar reactive components at concentrations consistent with experimental tests.

The specific mixture formulation includes:

- cylinder type and size;
- valve type;
- cylinder preparation instructions;
- components, their concentrations and the procedure for filling into the cylinder; and
- analysis/certification requirements.

These requirements shall be checked and approved by an authorized person independent of the formulation or production process.

The potential for the condensation of any of the components at the temperature of use shall be considered and taken into account in any calculations. Condensation shall be avoided.

7 Destructive or non-destructive testing

The feasibility of producing the gas mixture in an aluminium alloy cylinder shall be evaluated by conducting mixture composition analysis over time and establishing stability. Destructive tests followed by metallurgical examination are useful to support the decisions made on the basis of stability trials and confirm the compatibility between the aluminium alloy and the reactive gas.

In some cases a possible reaction producing hydrogen can be analysed and quantified. For low reactive halogenated gas concentrations this phenomenon is not a safety issue but can be used to establish mixture reactivity and stability.

8 Guidelines to perform the tests

The acceptance criteria for mixture feasibility are based on time and on the structural integrity of the cylinder. Tests shall be completed for both binary and multi-component reactive gas mixtures. The tests are valid for the aluminium alloy tested and shall be performed again at least if another alloy is used.

8.1 Current experience

Collect cylinder tests and stability data from previous mixtures manufactured. Evaluate the results using a statistical approach and base the results on the retesting of the cylinders containing the mixture to be approved.

8.2 Tests for new and higher concentration mixtures

Test mixtures shall be evaluated under controlled conditions. A validation procedure shall be undertaken for each new gas or mixture. It is recommended that tests:

- include cylinders filled above the maximum concentration required by the customer (for safety) and at the minimum concentration (for quality);
- be performed at the temperature, at which the cylinder will be exposed;
- be performed at the maximum pressure required for the mixture;
- provide information about the maximum acceptable moisture limit; and
- provide information about the maximum acceptable impurities of raw materials.

For new gases and higher concentration mixtures, it is recommended to plan tests to avoid safety risks (for example, increasing the test concentrations slowly in order to understand whether a reaction occurs).

Following these tests, considering the chemical analysis of the components introduced, or formed by reaction in the cylinders, complementary analyses shall be considered to improve knowledge about compatibility.

If a reaction between the gas, or mixture, and the cylinder occurs, a final cylinder burst test (at the test pressure of the cylinder) and a metallurgical examination shall be completed to establish the structural integrity of the cylinder and its safety for use. The burst test and metallurgical analysis shall be undertaken if the chemical analysis of the mixture has shown a significant decrease of the reactive halogenated gas concentration before the mixture reaches a stable concentration.

As a minimum, the feasibility study shall report on:

- aluminium alloy used;
- internal treatment of the cylinder under test;
- name and the concentration of the component tested;
- filling pressure of the test mixture;
- procedure used to prepare the mixture; and
- results of the tests (analysis data, internal cylinder inspection, metallurgical data, etc.).

Any other information required to enable the test to be repeated shall be documented in the report.

The objective of the test is to establish that there are no dangerous reactions between the internal cylinder walls and the reactive gas mixture and the filled cylinder is safe for use.

Visual inspection, hydraulic test, ultrasonic test, or other tests shall prove the acceptability of the result.

The preparation procedure for the mixtures in aluminium alloy cylinders shall be approved by a technically competent person (internally or externally) in the field of cylinders manufacturing technology and in the formulation/specification of specialty gas mixtures who has the responsibility of the opinion provided.

9 Cylinder selection

Control the pressure test and the material compatibility of the cylinder with respect to the mixture to be filled. Control the previous filling of the cylinders to establish the gas compatibility with the new gas to be filled.

The coating of the internal cylinder walls with protective liners can be considered.

10 Cylinder preparation

The cylinder shall be dried by suitable heating and by evacuation or other equivalent methods. The moisture in the cylinder shall be minimised and the concentration established by analysis or other means.

The final moisture concentration shall not exceed the value determined during the evaluation of the test mixture (see 8.2).

A residual pressure/non return valve should be fitted in order to avoid back flow and exposure of the internal cylinder walls to air during the use of the mixture.

11 Mixtures components purity and compatibility

The purity of all components shall be established to make sure that the mixture is compatible with the aluminium alloy internal cylinder surface according to the principles detailed in this procedure. Moisture is a key impurity which shall be minimised within the cylinder and all raw materials including the balance gases used. Any other impurities in the balance gas that can react with components in the mixture shall be considered.

12 Cylinder preparation before filling

Before filling a particular preparation of the internal walls may be required. This preparation may be done in different ways, for example:

- filling the cylinder with the same gas mixture that will ultimately be filled into the cylinder but at a lower filling pressure (for example, 3 bar) followed by evacuation; or
- treating the internal walls with some specific chemicals to passivate them.

The preparation shall be completed based on the procedure approved and feasibility tests performed.

13 Instability of production mixture

Analysis to validate the preparation should be done on all the cylinders. If the analysis shows that the concentration of the reactive component has decreased by an unacceptable value, an investigation shall be completed to explain the results.

14 Traceability

Records to maintain the traceability of the cylinder containing reactive gas mixtures is strongly recommended. This enables an assessment of the cylinder and components on return from the customer and allows the supplier to keep the cylinder in a similar service.

As a minimum the records shall show the type of components and their concentration for the previous mixture filled in the cylinder.

If traceability is not possible the cylinders should be dedicated to the service with the reactive gas mixtures and hard stamped with mixture and concentration contained.

15 Control and reuse of returned cylinders

Cylinders returned with residual pressure, may be reused after evacuation. Consider the risk of a blocked residual pressure/non return valve by corrosion.

If the cylinder is returned without residual pressure, internal procedures shall be in place to determine whether the cylinder may be returned to service and what level of testing and examination is required before it can be returned to service. The procedures should include the internal inspection of the cylinder.

A risk assessment shall be done to establish safety before changing the cylinder to another service.

A visual examination of the cylinder valve is recommended. If there is no pressure in the cylinder a leak check should be performed.

16 Residual mixture evacuation before the hydraulic retesting

Before performing a hydraulic re-test special care shall be taken to ensure that the cylinder is properly evacuated and purged, so that the residual gas is removed from the cylinder wall. The cylinder content shall be disposed safely.

Furthermore, particular care should be taken to ensure that the cylinder is dried quickly following hydraulic testing to avoid damage to the internal walls. An ultrasonic test may be performed instead of a hydraulic test.

After testing/re-testing of a cylinder which is to be used in reactive gas service the internal treatment/preparation shall be repeated to ensure that the cylinder surface has not been compromised by prior service and by the re-test procedure. Tests and procedures shall be in place to document and to provide verification of these activities.

17 Customer information to avoid contamination

Information should be provided to customers requesting that they leave residual pressure in the cylinder and avoid contamination (for example, using a cylinder label).

18 Audit guideline

It is recommended that facilities manufacturing reactive halogenated gas mixtures in aluminium alloy cylinders undergo periodic audits to assess their compliance with this publication and with other recognised safe working practices. The nature and detail of such audits shall be determined by the facilities level of involvement with reactive gas mixtures and compliance with local regulations.

The following checklist (see Table 1) contains a non-exhaustive list of items to audit. The *Reference section* column gives, where appropriate, the section of this publication where more information on the checklist item may be found.

Table 1 - Gas compatibility with aluminium alloy cylinders

Serial No.	Gas compatibility with aluminium alloy cylinders	Reference section
1	Is the manufacturing site approved for the manufacture of <u>reactive</u> halogenated gas mixtures by the technically competent company authority?	4
2	Is there a person designated as having overall responsibility for the formulation, review and approval of recipes?	4
3	Is there a system for the approval of new recipes?	6
4	Formulation of <u>reactive</u> halogenated gas mixtures shall be approved by at least one authorized person other than the creator of the formulation (checker)	6
5	Are data sources relevant to the <u>reactive</u> halogenated gas mixtures formulation available to the creators and checkers of the formulation?	6
6	Has a study to prevent condensation after manufacturing been conducted for each formulation?	6
7	There is a clear production procedure for the authorized <u>reactive</u> halogenated mixture?	6
8	There is a procedure detailing all of the steps to be followed for the mixture preparation?	6
9	The feasibility approval based on current experience has been done <u>taking into account cylinder tests and stability data from previous mixtures manufactured?</u>	8
10	The tests for a new preparation have been done above the maximum concentration required?	8
11	The feasibility study for a new preparation contains the information suggested in section 8?	8
12	Has a study to control the stability of the mixture been conducted for each <u>reactive</u> gas <u>mixture</u> ?	8
13	The cylinder preparation is done according to the procedures established during the feasibility test?	11
14	Are the impurities in the balance gas checked?	12
15	The results of the analysis are evaluated by a competent person to check if the mixture is acceptable?	14
16	The re-preparation is authorized by a competent person?	14
17	There is a cylinder traceability system in place?	15
18	There are controls on returned cylinders?	16
19	Before the hydraulic re-test the mixture is removed?	17
20	After the hydraulic re-test the cylinder is dried quickly?	17
21	The user is asked to leave residual pressure in the cylinder?	18

19 References

Unless otherwise specified, the latest edition shall apply.

- [1] ISO 11114-1 *Transportable gas cylinders - Compatibility of cylinder and valve materials with gas contents - Part 1: Metallic materials* www.iso.org
- [2] ISO 7866, *Gas cylinders – Refillable seamless aluminium alloy gas cylinders – Design, construction and testing* www.iso.org

**Appendix A - Gases not compatible with aluminium
according to ISO 11114-1 (Informative)***

Serial No.	Gas name	Remarks
5	Boron trichloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
6	Boron trifluoride	Mixtures containing less than 0.1 % BF ₃ may be filled into AA cylinders
**	<u>Carbonyl fluoride</u>	<u>See footnote</u>
20	Chlorine	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders
22	<u>Methyl chloride</u> (Chloromethane)	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
35	Dichlorosilane	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
46	Ethyl chloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
49	Fluorine	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders
58	Hydrogen bromide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
59	Hydrogen chloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
61	Hydrogen fluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
62	Hydrogen iodide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
69	Methyl bromide	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
83	Phosgene (Carbonyl Chloride)	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
90	Silicon tetrachloride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
91	Silicon tetrafluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
94	Sulphur tetrafluoride	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
96	Trichlorosilane	Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders
100	Tungsten hexafluoride	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders
101	Vinyl bromide	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders
102	Vinyl chloride	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders
103	Vinyl fluoride	Mixtures containing less than 0.1 % of this gas may be filled into AA cylinders

* NOTE: the ISO standard does not precise the units.

**NOTE: although carbonyl fluoride is not listed in ISO 11114-1, it is suggested to consider that in wet conditions, carbonyl fluoride is corrosive with most materials, particularly with aluminium alloys (hydrolyses to HF). Mixtures of dry gas not exceeding 0.1 % of this gas may be filled into AA cylinders.