REVIEW ANALYSIS OF INDIAN STANDARD

1. **Sectional Committee No. & Title: FAD 19, Dairy Products and Equipment**
2. **IS No.: IS 1825:1983**
3. **Title: Specification for Aluminium Alloys Milk Cans (*Second Revision*)**
4. **Date of Review: 2021**
5. **Review Analysis**

i) Status of Standard(s), if any from which assistance had been drawn in the formulation of this IS

Standard (No. & Title)	**Whether the standards has been revised**	**Major changes**	**Action proposed**
Assistance has not been taken from any other standards (No Records Found)			

ii) Status of standards referred in the IS

S. No.	**Referred standards (No. & Title)**	**IS No. of this standards since revised**	**Changes that are of affecting the standard under review**	**Action Proposed**
1	IS 1373: 1981 Title: Tinned Mild Steel Milk Cans (*Third Revision)*	Standard withdrawn	Since IS 1373: 1981 has been withdrawn and IS 16640: 2016 has been published, clause **0.4** of IS under review is highly affected	(*Page 3, Clause* ***0.4****, Lines 1,2,3 & 5*) – The sentence ‘In India, at present, milk cans in use are made of tinned mild steel, aluminium alloy and stainless steel. The Indian Standards ‘Specification for milk cans made of tinned mild steel’ (IS 1373: 1981) has already been published, but the standard covering stainless steel milk cans has been deferred, due to shortage of stainless steel’ *may be substituted by* ‘In India, at present, milk cans in use are made of aluminium alloy and stainless steel. The

				requirements for stainless steel milk cans are covered in IS 1664: 2016 'Stainless Steel Milk Cans-Specification'. This standard has been formulated to cover the requirements for aluminium alloy milk cans.'
2	IS 2: 1960 Title: Rules for Rounding off Numerical Values (*Revised*)	No Change	NA	None
3	IS 737: 1974 Title: Specification for Wrought Aluminium and Aluminum alloys, Bars, Sheet and Strip (for general engineering purposes) (*Second Revision*)	IS 737: 2008 Title: Wrought Aluminium and Aluminum alloys, Bars, Sheet and Strip for General Engineering Purposes)-Specification (*Fourth Revision*)	No changes observed in IS 737: 2008 which may affect IS under review	*(Page 4, Clause* ***3.1****, Line 3)* – Substitute 'IS: 737-2008' *for* 'IS 737-1974' *(Page 4, Clause* ***3.2****, Line 5)* – Substitute 'IS: 737-2008' *for* 'IS 737-1974' (*Page 4, footnote*) – Substitute the sentence 'Wrought aluminium and aluminum alloys, bars, sheet and strip for general engineering purposes)-Specification (*Fourth Revision*)' *for* 'Specification for Wrought Aluminium and Aluminum alloys, Bars, Sheet and Strip (for general engineering purposes) (*second revision*)'
4	IS 733: 1975 Title: Specification for Wrought Aluminium alloys, Bars, Rods and Sections (for general engineering purposes) (*Second Revision*)	IS 733: 1983 Title: Specification for Wrought Aluminium alloys, Bars, Rods and Sections (for general engineering purposes) (*Third Revision*)	No changes observed in IS 733: 1983 which may affect IS under review	(*Page 4, Clause* ***3.2****, Line 3*) – Substitute 'IS 733: 1983' *for* 'IS 733: 1975' (*Page 4, Clause* ***3.3****, Line 2*) – Substitute 'IS 733: 1983' *for* 'IS 733: 1975' (*Page 4, footnote)* – Substitute the sentence 'Specification for Wrought Aluminium alloys, Bars, Rods and Sections (for general engineering purposes) (*Third Revision*)' *for* 'Specification for Wrought Aluminium alloys, Bars, Rods and Sections (for general engineering purposes) (*Second Revision*)'
5	IS 1790: 1961	This standard has		*(Page 10, Clause* ***5.3****, Lines 3 and 4)* – Substitute the sentence 'The

	Title: Method for Brinell hardness test for light metals and their alloys	been withdrawn		Brinell hardness of the cans shall not be less than *85 HBW* when tested according to the method prescribed in IS: 1500: Part 1: 2019.' For 'The Brinell hardness of the cans shall not be less than *85 HB* when tested according to the method prescribed in IS 1790: 1961.' (*Page 10, footnote)* – Substitute the sentence 'Metallic materials - Brinell hardness test: Part 1 test method (Fifth Revision)' *for* 'Method for Brinell hardness test for light metals and their alloys'
6	IS 2927: 1975 Title: Specification for brazing alloys (*First Revision*)	No Change	NA	None
7	IS 812: 1957 Title: Glossary of terms relating to welding and cutting of metals	No Change	NA	None
8	IS 7273: 1974 Title: Method of testing fusion welded joints in aluminium and aluminium alloys.	No Change	NA	None
9	IS 4905: 1968 Title: Methods for random sampling	IS 4905: 2015 Title: Random sampling and randomization procedures (*First Revision*)	NA	(*Page 12, Clause* ***A-1.3.1****, Line 2*) – Substitute 'IS 4905: 2015' *for* 'IS 4905: 1968' (*Page 12, footnote)* – Substitute the sentence 'Random sampling and randomization procedures (*First Revision*)' *for* 'Methods for random sampling'
10	IS 1500: 2005 Title: Method for Brinell Hardness Test	This standard has been withdrawn	NA	Amendment No. 3 need to be replaced as IS 1500: 2005 has been withdrawn.

	for Metallic Materials			

iii) Any other standards available related to the subject & scope of the standard being reviewed (International/regional/other national/association/consortia, etc. or of new or revision of existing Indian Standards)

S. No.	Standards (No. & Title)	Provisions that could be relevant while reviewing the IS	Action proposed
1	IS 16440: 2016 Stainless steel milk cans - Specification	Marking clause (clause 7.1 and 7.2) and Testing clause (clause 7)	Marking clause and Testing clause of standard under review (IS 1825) may be updated as per marking and Testing clause of IS 16440: 2016
2	IS 1500: Part 1: 2019/ISO 6506-1: 2014 Metallic materials - Brinell hardness test: Part 1 test method (Fifth Revision)	The IS 1790: 1961 and IS 1500: 2005 referred in IS under review for measurement of Brinell hardness have been withdrawn.	The latest version of IS 1500 may be referred in the IS under review (IS 1825).
3	IS 1500: Part 2: 2013/ISO 6506-2: 2005 Matallic Materials - Brinell Hardness Test Part 2 Verification and Calibration Testing Machnies		
4	IS 1500: Part 3: 2019/ISO 6506-3: 2014 Metallic materials - Brinell hardness test: Part 3 calibration of reference blocks (Fifth Revision)		
5	IS 1500: Part 4: 2019/ISO 6506-4: 2014		

	Metallic materials - Brinell hardness test: Part 4 table of hardness values (Fifth Revision)		

iv) Technical comments on the standard received, if any

S. No.	Source	Clause of IS	Comment	Action proposed
1	BIS Licensee	1.1	Delivery type should also be allowed for 30 Litres, 40 Litres and 50 Litres as they are used in Bikes and will make easy to market too.	Specifications for delivery type aluminium milk cans with rated capacity 30 Litres, 40 Litres and 50 Litres may be incorporated in IS 1825: 1983.
2	BIS Licensee	5.0	Different types of lid design should be added i.e. Pull type lid and Lockable type lid.	Specifications for different types of lid design i.e. pull type and lockable type may be included in IS 1825: 1983.
3	BIS Licensee	5.9	The mass of 50 litre can including lid should be 7.1 kg.	Requirement for mass of 50 litre can may be changed from 8.0 kg to 7.1 kg.
4	BIS Licensee	NA	Regarding Raw Material, there should be thorough check in specification of Raw Material after supplies made to the consumers	None

v) Information available on technical developments that have taken place (on product/processes/practices/use/or application/testing/input materials, etc)

S. No.	Source	Development	Relevant clause of the IS under review that is likely to be impacted (Clause & IS No.)	Action Proposed
1	BIS Licensee	Delivery type should also be allowed for 30 Litres, 40 Litres and 50 Litres as they are used in Bikes and will make easy to market too.	Clause 1.1 (IS 1825)	Specifications for delivery type aluminium milk cans with rated capacity 30 Litres, 40 Litres and 50 Litres may be incorporated in IS 1825: 1983.

2	BIS Licensee	Different types of lid design should be added i.e. Pull type lid and Lockable type lid.	Clause 5.0 (IS 1825)	Specifications for different types of lid design i.e. pull type and lockable type may be included in IS 1825: 1983.
3	BIS Licensee	The mass of 50 litre can including lid should be 7.1 kg.	Clause 5.9 (IS 1825)	Requirement for mass of 50 litre can may be changed from 8.0 kg to 7.1 kg.
4	Research Papers	Aluminium is non-essential element for humans and is considered to be a toxic metal. Processing and storage of milk in aluminium containers also raise aluminium content significantly. Therefore, leaching /migration of aluminium alloy extract into the liquid milk is a matter of concern (Fink & Rohrman, 1932; Al Juhaiman, 2010).	Clause 7.0 (IS 1825)	Testing on leaching or migration of aluminium alloy extracts into the liquid milk may be included in IS 1825.
5	Research Papers	In strong contrast to its very mild action on the organs of the human body, the effect of milk on most metals is quite pronounced, in fact, the corrosion of metals by milk is one of the most serious corrosion problems facing modern civilization and industry. It has been known that milk in contact with iron and copper will not only acquire a metallic taste, but corrode these metals readily. Nickel, aluminum, and manganese aluminum alloys are not entirely satisfactory in high acid milk products. Furthermore, the nickel tarnishes readily and the aluminum is sensitive to	Clause 5.3 & 5.4 (IS 1825)	As per IS 1825, can body and can lid are to be anodized only if required by the purchaser. However, since, aluminium alloy milk cans are prone to corrosion by liquid milk, anodization of the can body and can lid are important and the same can be made mandatory.

		alkali washing powders. The group of tinned iron, copper, galvanized iron, iron, and zinc is unfit for use in contact with milk products. Milk is known to be a complex body containing both organic and inorganic radicals. Ordinary milk tends to be slightly acidic, having a pH at room temperature of 6.6-6.7 when sweet, to 4.6 when sour. It is evident, then, that unless extreme precautions are taken immediately after the milk is drawn from the cow, it will become slightly acidic due to the lactic acid produced by bacteria and will become more prone to corrosion (Fink & Rohrman, 1932).		

vi) Issues arising out of changes in any relevant IS or due to formulation of new Indian Standard

S. No.	**Related IS and its Title (revised or new)**	**Provision in the IS under review that would be impacted & the clause no. or addition of new clause/provision**	**Changes that may be necessary in the Standards under review**	**Action proposed**
1	IS 1373: 1981 Tinned Mild Steel Milk Cans (*Third Revision*)	This standard has been withdrawn which affects the clause 0.4 of IS 1825: 1983	*(Page 3, Clause* ***0.4****, Lines 1,2,3 5)* – The sentence 'In India, at present, milk cans in use are made of tinned mild steel, aluminium alloy and stainless steel. The Indian Standards 'Specification for milk cans made of tinned mild steel' (IS 1373: 1981) has already been published, but the standard covering stainless steel milk cans	Changes may be updated by technical committee

			has been deferred, due to shortage of stainless steel' *may be substituted by* 'In India, at present, milk cans in use are made of aluminium alloy and stainless steel. The requirements for stainless steel milk cans are covered in IS 1664: 2016 'Stainless Steel Milk Cans-Specification'. This standard has been formulated to cover the requirements for aluminium alloy milk cans.'	
2	IS 1500: 2005 Method for Brinell Hardness Test for Metallic Materials	This standard has been withdrawn which affects amendment 3 and clause 5.3 of IS 1825: 1983	Amendment No. 3 need to be replaced as IS 1500: 2005 has been withdrawn.	Changes may be updated by technical committee
3	IS 4905: 2015 Random sampling and randomization procedures (*First Revision*)	IS 4905: 1968 'Methods for random sampling' referred in IS under review has been changed to IS 4905: 2015 'Random sampling and randomization procedures (First Revision)'	*(Page 12, Clause* ***A-1.3.1****, Line 2)* – Substitute 'IS 4905: 2015' *for* 'IS 4905: 1968' (Page 12, footnote) – Substitute the sentence 'Random sampling and randomization procedures (First Revision)' for 'Methods for random sampling'	Changes may be updated by technical committee
4	IS 16440: 2016 Stainless Steel Milk Cans-Specification	This standard has been published while in clause 0.4 of IS 1825:1983, it has been written that the standard covering stainless	*(Page 3, Clause* ***0.4****, Lines 1,2,3,4 and 5)* – The sentence 'In India, at present, milk cans in use are made of tinned mild steel, aluminium alloy and stainless steel. The Indian Standards 'Specification for milk cans made of tinned mild steel' (IS 1373: 1981) has already been published, but the standard covering stainless steel milk cans has been deferred, due to shortage of stainless steel' *may be substituted by* 'In India, at present, milk	Changes may be updated by technical committee

		steel has been deferred. Publication of standard for stainless steel will affect the clause 0.4 of IS under review.	cans in use are made of aluminium alloy and stainless steel. The requirements for stainless steel milk cans are covered in IS 1664: 2016 ‘Stainless Steel Milk Cans-Specification’. This standard has been formulated to cover the requirements for aluminium alloy milk cans.’	

vii) **Any consequential changes to be considered in other IS**

S. No	Related IS to get impacted	Requirements to be impacted
1	IS 2342 : 1963 Specification for manually operated milk - Can washer	Clause 0.2, Line 7
2	IS 9854 : 2018 Code for construction of milk delivery vans (First Revision)	Clause 2 (References)
3	IS 170 : 2020 Acetone — Specification (Fifth Revision)	Clause 2 (Year and title of IS 1825: 1983 wrongly written in IS 170: 2020 under references clause)
4	IS 16440: 2016 Stainless Steel Milk Cans – Specification	Under Forward clause, line 7

6. Any other observation:

Based on observations from all the recently published standards:

(i) Title of the standard under review may be changed from “Specification for Aluminium Alloy Milk Cans” to “Aluminium Alloy Milk Cans – Specification”

(ii) A new clause of References containing all the references from 1 to 9 mentioned at 5 (ii) above may be incorporated after scope of the standard under review.

7. Recommendations:

The standard may be revised with

(i) All changes observed in standards referred in IS 1825 (Title and withdrawn)
(ii) Changes in marking clause as per IS 16440: 2016
(iii) Change in title format
(iv) New clause on referred standards
(v) Feedback/comments received from the BIS Licensees
(vi) Inputs obtained from research papers

Review Analysis of IS 1825: 1983 (Specification for Aluminum Alloy Milk Cans)

Bureau of Indian Standards (BIS) is going to revise IS 1825: 1983 as this standard has become very old. In this regard, all manufacturers of milk cans including BIS license may please suggest any thing that should be included or deleted from the standard.

Name and Address of your firm *

Geeta Industries (CM/L: 9600005912)
Plot No. 4, Johron, Kala Amb, Himachal Pradesh- 173030

Currently scope of this standard covers rated capacity of 20 litres for delivery cans; and rated capacity of 20 litres, 30 litres, 40 litres and 50 litres. Do you think that milk cans with other rated capacity can be added in the scope of this standards?? *

● Yes

○ No

If answer to question 1 is yes, then please suggest milk cans with what rated capacity should be included in scope of this standard and why?? *

DELIVERY TYPE SHOULD ALSO BE ALLOWED FOR 30LITRES, 40 LITRES AND 50 LITRES AS THEY ARE USED IN BIKES AND WILL MAKE EASY TO MARKET TOO.

What should be the minimum thickness at body and neck, bottom, lid (inner) and lid (outer) of the milk cans with rated capacity suggested by you in question no.1 ?? *

NOT REQUIRED

What should be the minimum mass in kg of the milk cans with rated capacity suggested by you in question no.1?? *

NO CHANGE

As per IS 1825:1983 materials used for manufacturing of milk cans shall conform to IS 737 and IS 733. Do you think that any other materials can be used for manufacturing of milk cans. If yes, which material and as per which IS. *

OK

Does this standard require any modifications in minimum thickness of milk cans with different rated capacity. If yes, please suggest the minimum thickness for different rated capacity. *

NO CHANGE REQUIRED

Does this standard require any modifications in minimum mass of the milk cans with different rated capacity. If yes please suggest the minimum mass in kg for milk cans with different rated capacity. *

NO CHANGE REQUIRED

Does this standard require any modifications in Testing parameters. If yes, please suggest the additional parameters that can be included in the standard. *

NO CHANGE REQUIRED

Does this standard require any modifications in marking clause. If yes, please mention the additional thing that should be included in marking clause. You can mention all particulars that should be marked on the milk cans. *

NO CHANGE REQUIRED

Any technical comments on IS 1825: 1983/ Recommendation

DIFFERENT TYPES OF LID DESIGN SHOULD BE ADDED I.E. PULL TYPE LID AND LOCKABLE TYPE LID

Review Analysis of IS 1825: 1983 (Specification for Aluminum Alloy Milk Cans)

Bureau of Indian Standards (BIS) is going to revise IS 1825: 1983 as this standard has become very old. In this regard, all manufacturers of milk cans including BIS license may please suggest any thing that should be included or deleted from the standard.

Name and Address of your firm *

Bimal Industries Unit-II (CM/L: 9950807)
Plot No. 2, Industrial Area, Kala Amb, Sirmaur, Himachal Pradesh

Currently scope of this standard covers rated capacity of 20 litres for delivery cans; and rated capacity of 20 litres, 30 litres, 40 litres and 50 litres. Do you think that milk cans with other rated capacity can be added in the scope of this standards?? *

○ Yes

● No

If answer to question 1 is yes, then please suggest milk cans with what rated capacity should be included in scope of this standard and why?? *

NA

What should be the minimum thickness at body and neck, bottom, lid (inner) and lid (outer) of the milk cans with rated capacity suggested by you in question no.1 ?? *

NA

What should be the minimum mass in kg of the milk cans with rated capacity suggested by you in question no.1?? *

NA

As per IS 1825:1983 materials used for manufacturing of milk cans shall conform to IS 737 and IS 733. Do you think that any other materials can be used for manufacturing of milk cans. If yes, which material and as per which IS. *

no option

Does this standard require any modifications in minimum thickness of milk cans with different rated capacity. If yes, please suggest the minimum thickness for different rated capacity. *

in 50 ltr

Does this standard require any modifications in minimum mass of the milk cans with different rated capacity. If yes please suggest the minimum mass in kg for milk cans with different rated capacity. *

in 50 ltr weight should be 7.100 kg

Does this standard require any modifications in Testing parameters. If yes, please suggest the additional parameters that can be included in the standard. *

NA

Does this standard require any modifications in marking clause. If yes, please mention the additional thing that should be included in marking clause. You can mention all particulars that should be marked on the milk cans. *

NA

Any technical comments on IS 1825: 1983/ Recommendation

NA

Review Analysis of IS 1825: 1983 (Specification for Aluminum Alloy Milk Cans)

Bureau of Indian Standards (BIS) is going to revise IS 1825: 1983 as this standard has become very old. In this regard, all manufacturers of milk cans including BIS license may please suggest any thing that should be included or deleted from the standard.

Name and Address of your firm *

BIMAL ALUMINIUM PVT LTD, 35 INDUSTRIAL ESTATES-II,YAMUNA NAGAR,HARYANA INDIA

Currently scope of this standard covers rated capacity of 20 litres for delivery cans; and rated capacity of 20 litres, 30 litres, 40 litres and 50 litres. Do you think that milk cans with other rated capacity can be added in the scope of this standards?? *

○ Yes

● No

If answer to question 1 is yes, then please suggest milk cans with what rated capacity should be included in scope of this standard and why?? *

NA

What should be the minimum thickness at body and neck, bottom, lid (inner) and lid (outer) of the milk cans with rated capacity suggested by you in question no.1 ?? *

NA

What should be the minimum mass in kg of the milk cans with rated capacity suggested by you in question no.1?? *

NA

NA

As per IS 1825:1983 materials used for manufacturing of milk cans shall conform to IS 737 and IS 733. Do you think that any other materials can be used for manufacturing of milk cans. If yes, which material and as per which IS. *

NA

Does this standard require any modifications in minimum thickness of milk cans with different rated capacity. If yes, please suggest the minimum thickness for different rated capacity. *

NA

Does this standard require any modifications in minimum mass of the milk cans with different rated capacity. If yes please suggest the minimum mass in kg for milk cans with different rated capacity. *

NA

Does this standard require any modifications in Testing parameters. If yes, please suggest the additional parameters that can be included in the standard. *

NA

Does this standard require any modifications in marking clause. If yes, please mention the additional thing that should be included in marking clause. You can mention all particulars that should be marked on the milk cans. *

NA

Any technical comments on IS 1825: 1983/ Recommendation

NA

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ORIGINAL ARTICLE

Estimating Aluminum leaching from Aluminum cook wares in different meat extracts and milk

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KEYWORDS

Al cook wares;
Al leaching;
Meat extract;
Milk;
Weight loss;
Provisional Tolerance Weekly Intake (PTWI);
Polarization methods

Abstract A method of estimating Al leaching from Al cook ware in some meat extracts and liquid milk was investigated. In the present work four kinds of Al cook wares from four countries were chosen from the local market. Extracts of boiled meat (lamb, chicken, and fish) were used to make 10–50% (w/v) concentrations. In addition liquid fresh milk and long life milk were diluted to make 10–50% (v/v) concentrations. Weight loss (WL) method, atomic absorption, polarization method, and surface study were applied. The "estimated" Al intake per person from WL in 30% meat extract and milk range from 8.16 to 12.75 mg/h with fish extract having the highest leaching and chicken extract having the lowest leaching. Atomic absorption gave comparable results to that of WL. Comparing the present results with the Provisional Tolerance Weekly Intake of Al approved by the FDA/WHO shows that Al leaching from Al cook wares may add high doses of Al into the diet.

1. Introduction

Aluminum is a non-essential metal to which humans are frequently exposed. Al can be toxic when injected directly to animals (Slanina and Falkeborn, 1984) or accidentally to humans as in the case of dialysis (Gitelman, 1989). Aluminum was regarded a neurotoxin agent since 1980 (Gitelman, 1989). Due to its accumulation in brain, bones, and liver Al was associated with some diseases like dialysis encephalopathy and bone disorder (Winship, 1993; Yokel, 1994). There is a continuing interest of Al content in food and its possible relation to Al toxicity especially to the elderly and to people with kidney failure (Winship, 1993; Fimreite et al., 1997; Soni et al., 2001; Ščančar et al., 2004).

Sources of Al entering the human body include food, water, beverages, cosmetics, medicines, food additives, and Aluminum leaching from Al cook wares. There is some disagreement about using Al cook wares in cooking. Some studies regard using Al utensil and Al foils safe for cooking (Ranau et al., 2001; Soni et al., 2001; Verissimo et al., 2006). Other studies regard them hazardous and do not advice using them especially in acidic food (Ščančar et al., 2004; Al-Mayouf et al., 2008; Fimreite et al., 1997). In Saudi Arabia there are a few studies which relate the daily habits of Al consumption with

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Al toxicity. An earlier study correlates Aluminum in blood serum for elementary school girls with the daily habits (Al-Saleh and Shinwari, 1996).

It is well established that Al dissolution is highly dependent on pH, temperature, and the presence of complexing agents. Al exhibits a passive behavior in aqueous solutions due to the protective compact Al_2O_3 film on its surface. However, the solubility of this protective film increases in acidic and alkaline medium. According to Bi (1996), Al leaching in aqueous solutions may be explained by the following chemical reaction occurring on the surface of the Al cookware:

$$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O$$

The free Al ions in solution react with organic acids and other complexing agents found in food.

There is a continuous use of Al cook wares in different countries including Saudi Arabia despite its association with serious health problems. Thus the aim of this work is to shed some light on Al leaching in aqueous solutions containing meat extracts and liquid milk using different kinds of Al cook wares brought from the local market.

2. Materials and methods

2.1. Materials

Four kinds of Al cook wares were chosen from the local market from four different countries China, India, Syria, and Saudi Arabia. The samples were named S, Y, I, and C to avoid any misconceptions. In addition pure Al of 99.999% (from Good fellow, England) was used for comparison. Ground meat of lamb, chicken and fish were used from the local market. The liquid full cream milk (fresh and long life) was diluted to the desired concentrations to make 10–50% (v/v) solutions.

2.2. Weight loss method

In the present work weight loss method (WL) at 90 °C was used to study Al leaching in aerated food extract solutions as follows:

1. The four different Al cook wares were cut into rectangular specimens of dimensions 2×2.5 cm and 2 mm thickness. The average exposed area was 11.80-cm^2 ± 0.20. These specimens were treated in the following method prior to each experiment. Wet polishing with SiC up to 1200 grade, washing with distilled water, then ultrasonic cleaning in acetone (ultrasonic cleaner from Cole Palmer) for 2 min before drying.
2. Ground meat of lamb, chicken, and fish were weighed to make stock solutions of 50% (w/v). Then they were boiled in distilled water at 90 °C for 1 h to get the meat extract. Filtration of the meat extract solutions was followed by dilution to obtain the 50% (w/v) which was kept in the fridge for a maximum of 1 week before use.
3. The Al samples were weighed in a balance (±0.0001 g from Mettler Toledo) then immersed in the hot meat extract at 90 °C for 1 h. All experiments were performed in aerated solutions and maintained at 90 °C ± 1.
4. After the leaching experiments the Al samples were immersed in a hot cleaning solution of CrO_3 + H_3PO_4 at 80 °C for 7 min to remove the reaction products from the surface. Finally, it was washed generously with distilled water then acetone. The dry Al sample was weighed again to determine the weight loss. All WL experiments were performed in duplicates. The pH of the meat extract was measured before and after the experiments.

2.3. Atomic absorption method (AA)

The remaining solutions after WL experiments were analyzed by AA technique using an instrument from Shimadzu (A.A. 6701F) to determine the amount of dissolved Al^{3+}.

2.4. Electrochemical method

This method was applied to estimate small changes of Al leaching using a sample holder (from Radiometer) connected to a galvanostat/potentiostat (from ACM). The Al cook wares were cut into circular disks of 1.4 cm diameter and an exposed area of 1.13 cm^2. The Al disk (as the working electrode) was fitted into a thermo stated sample holder cell. The reference electrode was SCE and the auxiliary electrode was Platinum. All electrochemical experiments were performed in aerated solutions and maintained at 60 °C ± 1 using a circulating water bath (from Haak). After performing open circuit potential for 1 h, polarization measurements were done to obtain corrosion current density from Tafel method.

2.5. Surface study

The surface morphology and surface analysis of Al samples were studied using scanning electron microscope (SEM) from (Joel-JSM-6060LV) connected with energy dispersion X-ray (EDX).

3. Results and discussion

3.1. Weight loss method

Although WL is an old technique, it is used to simulate Al leaching from Al cook wares. It is cost effective, quick, and environmentally friendly. The remaining of meat (mostly fibers) had little effect on Al leaching. An experiment of the WL method of the whole meat at 50% concentration was compared to the meat extract at 50% concentration and the difference was 2.7% only.

Corrosion rate (CR) from WL method was calculated using the following equation:

$$\text{Corrosionrate} = \frac{\Delta w}{A \times t}$$

where Δw is the weight loss of Al alloy (mg) or the leaching amounts; A is the surface area (cm^2), and t is the immersion time (h).

CR in meat extracts and milk are listed in Tables 1 and 2. It is clear that there is a difference in Al leaching depending upon the composition of Al alloy which reflects the effect of alloying elements. It is shown from Tables 1 and 2 that the amount of Al leaching generally increased with increasing the concentration of meat extract.

Table 1 CR of Al from WL after immersion for 1 h at 90 °C in different concentrations of meat extracts.

Soln. extract	Al alloy	Conc. CR × 10^2 (mg/cm^2 h)				
		10% pH 6.73 pH 6.6	20% (w/v) pH 6.58	30% (w/v) pH 6.49	40% (w/v) pH 6.44	50% (w/v) pH 6.39
Lamb	C	2.43	3.28	3.25	3.31	3.45
	I	3.33	3.63	4.17	4.95	5.58
	S	1.91	2.53	2.85	3.35	4.53
	Y	2.33	2.73	3.01	3.21	3.43
		10% pH 6.55 pH 6.6	20% (w/v) pH 6.40	30% (w/v) pH 6.31	40% (w/v) pH 6.27	50% (w/v) pH 6.22
Chicken	C	2.23	2.65	2.72	2.68	2.71
	I	2.73	2.66	3.25	3.26	3.25
	S	2.41	2.31	2.78	2.71	2.72
	Y	2.53	2.28	3.00	2.86	3.11
		10% pH 6.92 pH 6.6	20% (w/v) pH 6.79	30% (w/v) pH 6.71	40% (w/v) pH 6.66	50% (w/v) pH 6.62
Fish	C	3.35	4.25	4.25	4.58	4.88
	I	3.45	4.09	4.14	3.86	4.16
	S	3.35	3.11	3.68	3.82	4.66
	Y	2.87	2.70	2.73	2.94	3.63

Table 2 CR of Al from WL after immersion for 1 h at 90 °C in different concentration of milk.

Soln.	Al alloy	Conc. CR × 10^2 (mg/cm^2 h)				
		10% pH 7.3	20% (w/v) pH 7.2	30% (v/v) pH 7.1	40% (w/v) pH 6.9	50% (w/v) pH 6.8
Fresh milk (F. Milk)	C	3.16	3.03	4.08	4.04	5.08
	I	2.30	3.26	3.43	3.81	5.49
	S	1.64	2.44	2.40	2.60	3.65
	Y	2.17	2.24	2.12	2.26	2.34
Long life milk (L. Milk)	C	3.72	3.55	3.62	3.58	3.86
	I	3.66	3.48	3.50	3.63	3.72
	S	2.33	2.44	2.60	2.78	2.95
	Y	2.31	2.97	3.25	3.16	3.73

To compare the present data with the Provisional Tolerance Weekly Intake (PTWI) of 7 mg of Al/kg body weight of adult (World Health Organization, 1989), some assumptions are made. Assuming a family of 4 persons using an Al utensil of medium size with a diameter 20 cm and height 15 cm, the internal area of the Al utensil exposed to leaching will be about 1200 cm^2. The concentration of 30% for lamb (alloy C) is taken as an example and Al leaching per hour will be equivalent to:

$$3.25 \times 10^{-2} \frac{\mathrm{mg}}{\mathrm{cm}^2\,\mathrm{h}} \times 1200\ \mathrm{cm}^2 = 39.0 \frac{\mathrm{mg}}{\mathrm{h}}\ \text{Al per family}$$

$$= \frac{39.0\ \mathrm{mg\ Al/h}}{4\ \text{persons}}$$

$$= 9.75 \frac{\mathrm{mg}}{\mathrm{h}}\ \text{Al per person}$$

The "estimated" Al intake per person in mg/h from WL in 30% of meat extract and milk is shown in Figs. 1 and 2.

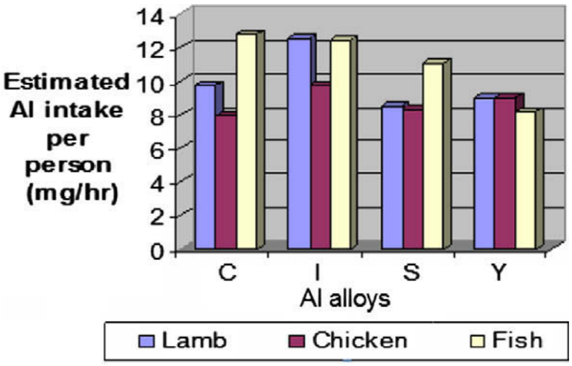

Figure 1 Estimated Al intake per person from WL in 30% meat extracts solutions in different Al alloys.

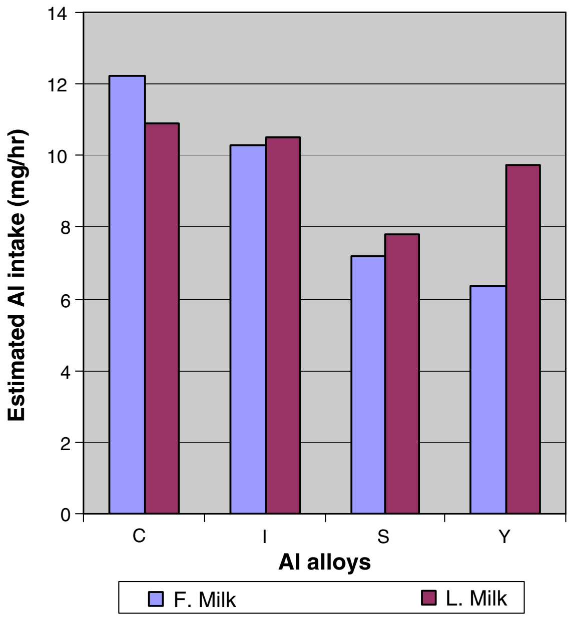

Figure 2 Estimated Al intake per person from WL in 30% milk solutions in different Al alloys.

From these results the order of Al leaching in 30% solutions appears to be:

fish > lamb > fresh milk ~ long life milk > chicken

In general for 30% concentrations there is a difference in Al leaching among the four different alloys with alloy I having the highest leaching and alloy Y having the lowest leaching. There is a difference in Al leaching depending upon the composition of Al alloy which reflects the effect of alloying elements. It is found from this study that fish extract appears to leach more Al than lamb or chicken. This shows that the composition of food determine the amount of Al leaching which agrees with others (Ščančar et al., 2004).

WL method simulates the amounts of Al leached by food in conditions close to the real ones. Distilled water was used in this study but it is expected that Al leaching from Al utensil using tap water will leach more Al as found from a previous study (Al Juhaiman, 2000). In real life during cooking people may add tomato paste, lemon juice, table salt, and other spices which were shown by many researchers to leach more Al when using Al utensils (Verissimo et al., 2006; Joshi et al., 2003).

No significant differences in pH were found in the present work. This finding agrees with other studies (Fimreite et al., 1997; Neelam and Kaladhar, 2000). The amino acids in meat and lactic acid in milk have high susceptibility to react with A^{3+} to form Aluminum complexes. The dissolution of Aluminum may change the local pH in Aluminum surface but it did not affect the pH of the solution which is measured by the pH meter. The pH range of the present study was almost neutral. In neutral solutions the protective Al_2O_3 film has low solubility. The solubility of the protective oxide film will increase as the pH decreases as was found by some researchers (Lenderink et al., 1993). Thus it is expected that Al leaching in meat and dairy products will be increased when the pH becomes low as in real cooking when adding lemon juice or tomato paste. This was also shown in a previous study of corrosion of Al in carboxylic and amino acids where the amount of Al leaching increased twice when the pH changed from 6.5 to 4.5 (Al Juhaiman et al., 2004; Al-Mayouf et al., 2008).

Even boiling water in Al cook wares resulted in leaching some Al into the medium, which was explained by the presence of fluoride (Neelam and Kaladhar, 2000). However this finding was completely opposed by another recent study where they showed that boiling water in Al utensils may reduce Al leaching in cooking by 60% (Karbouj and Nrtier, 2009).

The other controversial study reported that Al leaching was reduced by the presence of amino acids and that food stuff with neutral pH and low salt content like milk do not leach Al (Severus, 1989). Based on the present results there are appreciable amounts of Al leaching from milk ranging from 6.36 to 12.24 mg/h for 30% solutions for the different Al alloys. In addition, there was a significant Al leaching by pure amino acids (aspartic and glutamic acids) which was pH dependant (Al Juhaiman et al., 2004).

The safety of Al depends on whether it is absorbed or not and there are conflicting reports about its bioavailability (Prescott, 1989; Slanina and Falkeborn, 1984; Gitelman, 1989; Winship, 1993). A study of the average Al concentration in daily diet (Soni et al., 2001) showed that under normal circumstances the average dietary intake of Al (without water) is about 6–15 mg/day. In another report the total estimated average daily Al intake in USA was 26.5 mg/day (World Health Organization, WHO/FAO, 1989). The joint FAO/WHO Expert committee on food additives has established the Provisional Tolerance Weekly Intake (PTWI) of 7 mg of Al/kg body weight of adult (WHO/FAO, 1989). Based on the present results there are appreciable amounts of Al leaching from meat extract and milk ranging from 8.16 to 12.75 mg/h for 30% solutions for the different Al alloys. This amount will be increased with increasing concentration as shown in Tables 1 and 2. Using Al cook wares may leach significant amounts of Al into the food, which raise the amounts of Al to high levels and may be dangerous to children, the elderly and people with kidney problems.

3.2. *Atomic absorption measurements*

Analysis of dissolved Al^{3+} ions in the remaining solutions from WL experiments by AA are calculated in ppm (mg/L). As an example only 30% solutions of Fish and F. Milk were analyzed by AA. To compare the AA results with WL data the results from AA were multiplied by the volume of solution then divided by the area of Al sample and the time of leaching experiment of 1 h. The same earlier assumption was applied to calculate the "estimated" Al intake per person in mg/h from AA. The results of WL and AA are shown in Figs. 3 and 4. A good consistency was observed between the data from WL and AA. Using AA for analysis after WL is an uncommon method in the literature. Yet it was shown in this study and in a previous study that WL and AA gave comparable results (Al Juhaiman et al., 2004; Al-Mayouf et al., 2008).

3.3. *Electrochemical method*

The purpose for using this method is to detect any small changes in Al leaching. However it does not reflect the natural tendency of Al dissolution as WL. In these experiments the concentrations of meat and milk extracts were kept. All

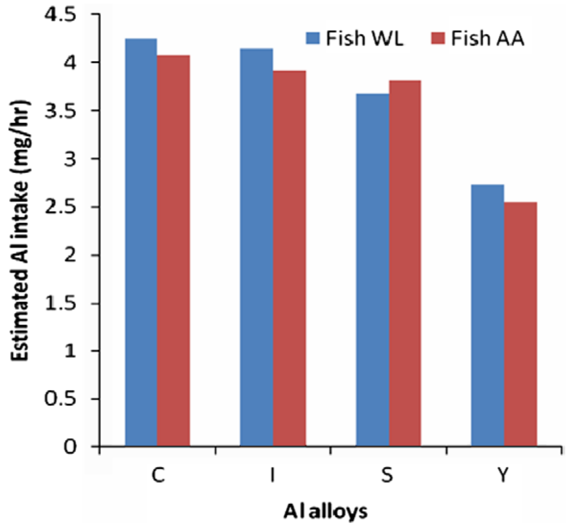

Figure 3 Comparison of Al leaching from WL and AA in 30% fish extracts in different Al alloys.

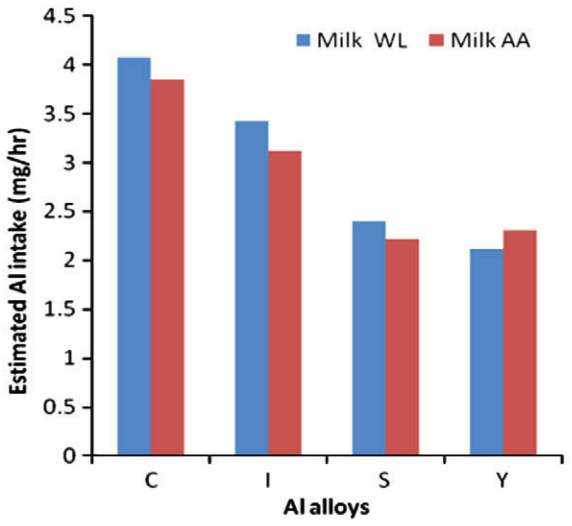

Figure 4 Comparison of Al leaching from WL and AA in 30% fresh milk in different Al alloys.

experiments were performed in aerated solutions at 60 °C ± 1. As an example only the solutions of 30% fish extract and the fresh milk was used. After running open circuit potential for an hour to attain equilibrium (not shown), Tafel plots were performed. The results are shown in Figs. 5 and 6.

The electrochemical parameters of Al in these solutions are listed in Table 3. It is shown from Table 3 that values of current density (I_{corr}) are in general less than 0.50 µA/cm^2. These low values may be explained because of the low temperature which is the maximum allowed temperature for electrochemical measurements. Thus it is expected that these current density data will be doubled or tripled when the temperature is increased to 100 °C as in real cooking.

From Tafel results the order of Al leaching of Al alloys in fish and milk solutions appeared to be:

Y > C > I > P > S

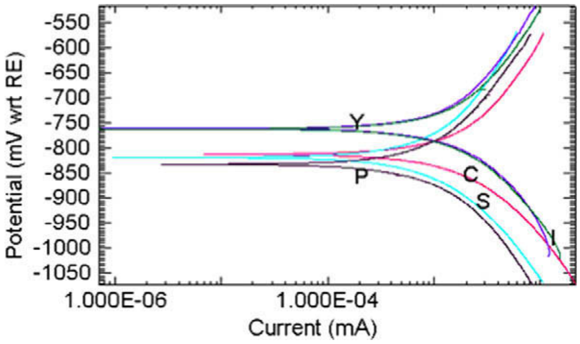

Figure 5 Tafel plot of 30% fish extract in pure Al and in different Al alloys at 60 °C.

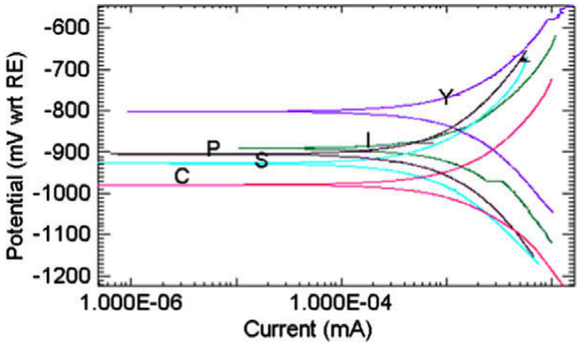

Figure 6 Tafel plot of 30% fresh milk in pure Al (P) and in different Al alloys at 60 °C.

It is surprising that alloy S leach less than pure Al in fish extract and fresh milk. This clearly reflects the role of alloying and shows that some alloying element may reduce Al leaching.

3.4. Surface study

Using EDX the Al composition was found to range between 97.2% and 98.6% Al with different alloying elements. Alloy S is chosen as an example of Al alloys after leaching experiment for 1 h. Washing the sample with distilled water and magnifying the surface in SEM in 30% fish extract (Fig. 7) showed some holes due to dissolution of Al by fish extract constituents. The same result was shown for 30% milk solution where the white area is partially milk constituent (Fig. 8). These results show that the amino acids in meat and lactic acid in milk have high susceptibility to react with A^{3+} to form Aluminum complexes.

4. Conclusion

This method allows us to estimate Al leaching from Al cook wares in meat extracts and milk at any concentration; it is reliable and simulates Al leaching from Al cook wares. Leaching of Al depends on solution composition, concentration and Al composition (alloying elements). In the present study WL and AA gave comparable results. Based on the present results it is estimated that using Al cook wares may leach significant amounts of Al into the food. This raises the amounts of Al

Table 3 Electrochemical parameters of Al alloys in 30% (w/w) fish extracts (pH 6.4) and 30% (v/w) milk (pH 7.0) at 60 °C.

30% Food extract	Al alloy	$-E_{\mathrm{corr}}$ (mV/dec.)	B_a (mV/dec.)	$-B_c$ (mV/dec.)	I_{corr} (μA/cm^2)
Fish	Pure Al	823	82.7	74.2	0.35
	C	822.4	86.7	69.5	0.41
	I	771.0	82.54	69.2	0.38
	S	819.3	89.67	69.2	0.23
	Y	767.4	103.3	83.9	0.47
Fresh milk	Pure Al	902.5	80.4	68.1	0.27
	C	980.2	77.5	65.6	0.28
	I	891.5	96.8	90.6	0.38
	S	835.2	66.4	57.5	0.22
	Y	796.4	70.8	59.6	0.26

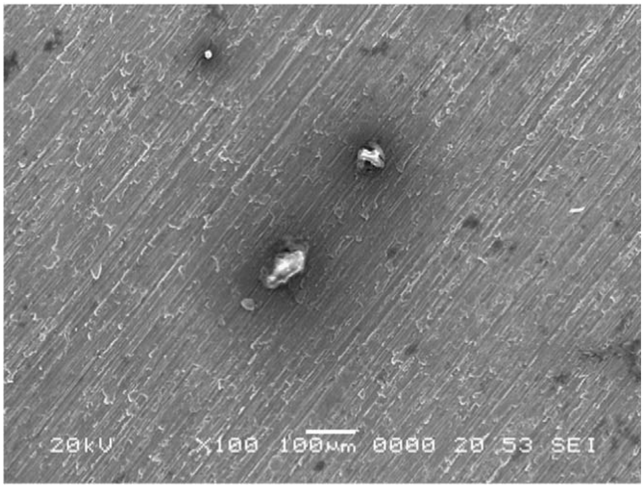

Figure 7 SEM of alloy S after leaching in 30% fish extract at 90 °C, 1 h.

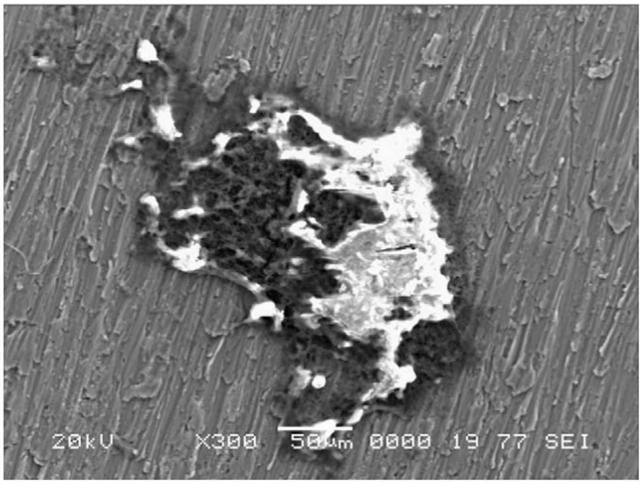

Figure 8 SEM of alloy S after leaching in 30% fresh milk at 90 °C, 1 h.

to high levels and may exceed the recommended amounts set by WHO/FAO. Therefore, continuous monitoring of Al level in daily diet, water, medicines, and food additives is recommended.

Conflict of interest statement

The author declares that there are no conflicts of interest.

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Aluminium Content in Milk and Milk Products and its Leachability from Dairy Utensils

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ABSTRACT

Aluminium is non-essential element for humans and is considered to be a toxic metal. The present investigation was carried out to determine aluminium concentrations in milk and milk products, to estimate the intake of aluminium via consumption of milk and dairy products and to investigate the leachability of aluminium from utensils into milk products during processing and storage. A total of 85 milk and milk products samples were collected from farms, individual farmers and dairy shops in Beni-Suef governorate, Egypt. Mean aluminium concentrations in farm milk, market milk, kareish cheese, yoghurt and rice pudding were 19.93, 107.32, 52.36, 4.19 and 80.97 ppm, respectively. Aluminium intake through milk and milk products consumption was calculated to be 246.72 mg week^{-1} which corresponds to 205.5% of the PTWI. Processing and storage of milk in aluminium containers also raise aluminium content significantly. The results indicated the advantage of using stainless steel over aluminium utensils for processing and storage of milk products, especially those acidic in nature.

Key words: Milk, aluminium, leaching, daily intake

INTRODUCTION

Aluminium is the third most abundant element in the environment, comprising 8.13% of the earth's crust. It is present naturally in soil, minerals and rocks and even in water and food. It does not appear to serve any essential biological function in the human body (Soni *et al*., 2001). The health safety of aluminium intake has long been a subject of controversial debate. For many years, it was not considered harmful to human health because of its relatively low bioavailability and its excretion in the urine is very efficient (Stahl *et al*., 2011). Recently, it has been associated with anaemia, osteomalacia and a neurological syndrome, commonly known as dialysis encephalopathy particularly in patients with chronic renal failure. In addition, there is evidence that aluminium is a cofactor in the development of serious brain disorders like Alzheimer's disease (Karbouj *et al*., 2009).

Humans are frequently exposed to aluminium, primarily from foods, water, airborne dust and pharmaceuticals (Semwal *et al*., 2006). Data from several countries summarized that adults are exposed to between 2 and 160 mg aluminium per day from various sources (Soni *et al*., 2001). Food is unquestionably the main source of aluminium intake. Aluminium enters the food chain through a number of natural and anthropogenic sources. The main sources of aluminium in the diet are cereal, desserts, beverages and milk products (Arruda *et al*., 1994).

Milk and milk products provide good quality nutrients necessary for a strong body and mind. However, the presence of toxic elements such as aluminium in milk and milk products may create health problems, especially for infants, children and old people who consume large quantity of those products (Gonzalez-Weller *et al*., 2010). Aluminium enters the milk and milk products from a variety of sources. Milk gets contaminated before milking, from the feed and fodder fed to the dairy cows. Additionally aluminium can be introduced into the milk and milk products during the production process or by contamination from the metal processing equipment (Soni *et al*., 2001; Deeb and Gomaa, 2011). The use of aluminium utensils for processing and storage of milk may increase substantially the level of this metal in milk and milk products (Semwal *et al*., 2006) and leaching of this metal from utensils is influenced by the quality of the containers, pH level, preparation conditions and the presence of complexing agents (Al Juhaiman, 2010).

The increasing demand of environmental and food safety has stimulated research regarding the risk associated with environmental contamination and consumption of foods contaminated with aluminium. As information on the levels of aluminium in milk and milk products in Egypt and on leaching of aluminium from processing utensils is scanty. Moreover, an additional insight into metal uptake and assessment of human risks associated with the consumption of milk and milk products are still needed. Therefore, this study was conducted to quantify the levels of aluminium in milk and milk products, to estimate the daily intake of this element through consumption of milk and milk products and to investigate the leachability of aluminium from utensils into milk products during processing and storage.

MATERIALS AND METHODS

Collection and preparation of samples: A total of 85 milk and milk products samples (15 farm milk, 15 market milk, 20 kareish cheese, 20 yoghurt and 15 rice pudding) were collected from local farms, individual farmers and dairy shops in Beni-Suef governorate, Egypt. All samples were collected in nitric acid-washed polyethylene containers. The samples were immediately transported to the laboratory in a cooler with ice packs and were stored at -20°C until analysis.

Milk and milk product samples (2 mL or g) were digested with nitric and perchloric acid mixture (HNO_3: $HCLO_3$ = 4:1 v/v) until a transparent solution was obtained (Patra *et al*., 2008). After digestion, samples were filtered and diluted to a suitable concentration. Three blank samples, where biosample was substituted by de-ionized triple distilled water, were run simultaneously with each batch of the digestion. Working standard solutions were made up by dilution of certified standard solutions to the desired concentration. All reagents used were of analytical reagent grade. Ultra high purity water was used for all dilutions. All glass and plastic wares were washed and kept overnight in 10% (v/v) nitric acid solution. Afterwards, it was rinsed thoroughly with ultra-pure water and dried.

Sample analysis: The Al content of the digested samples was determined using flame atomic absorption spectrophotometer (Thermo Solaar M6 A.A. spectrometer, Thermo Electron). The instrumental parameters for Al were: Wave length 309.3 nm, bandpass 0.5 nm, lamp current 100% and nitrous oxide-acetylene flame.

Estimated Daily Intake (EDI): The daily intake of Al for an adult person (60 kg b.wt.) was calculated as follows:

$$\text{EDI} = \frac{C_{\text{metal}} \times W_{\text{food}}}{\text{Body weight (b.wt.)}} (\text{mg/kg b.wt./day})$$

where, C_{metal} (mg kg^{-1}, on fresh weight basis) is the concentration of Al in contaminated foods, W_{food} represents the daily average consumption of food and b.wt. represents the body weight. The average daily consumption per adult person were considered to be 200 mL, 22, 14 and 106 g of milk, kareish cheese, yoghurt and rice pudding, respectively (Saleh *et al*., 1998; FAO., 2009; Al-Ashmawy, 2011).

Experimental study: Milk, yoghurt and kareish cheese were processed individually in aluminium and stainless steel utensils to determine the leaching of aluminium from dairy utensils. Raw milk (5 L) was divided into 5 equal parts. The first part was set as a control (raw milk, analyzed before processing). The second and third parts were individually heated to boiling temperature for 10 min in aluminium and stainless steel utensils while the fourth and fifth parts were separately stored at 4°C for 24 h in aluminium and stainless steel utensils.

Two batches of yoghurt were prepared (one batch in aluminium cookware and the other batch in stainless steel cookware). Raw cow's milk (1.5 L) was heated in a water bath at 90°C for 30 min, cooled to about 42°C and inoculated with 2% of yoghurt starter cultures (Yoflex, Chr. Hansen). The inoculated milk was incubated at 43°C until a firm coagulum was formed (5 h).

In the same manner, two batches of kareish cheese were prepared (one batch in aluminium cookware and the other batch in stainless steel cookware). It was prepared by incubation of raw milk (1.5 L) at 30°C for 2 h, followed by rennet addition and further incubation until coagulation. After that, the curd was salted (5 g/100 mL original milk) while ladling into cheesecloth's for overnight drainage of the whey.

Raw milk, boiled milk, cold stored milk, yoghurt and kareish cheese samples were collected in nitric acid-washed polyethylene containers. The samples were stored at -20°C until analysis. All analyses were performed in duplicate.

Data analysis: Concentrations were expressed as Mean±Standard Error (SE), minimum and maximum values. All calculations were performed with the SPSS pocket program for windows (version 16, 2007). One-way analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine significant differences in the measured attributes at $p<0.05$.

RESULTS AND DISCUSSION

The aluminium contents of milk and milk products are given in Table 1. Significant levels of aluminium were detected in all the samples analyzed. The levels of aluminium in the farm milk samples were between 0.51 and 104.93 ppm, with a mean value of 19.93±7.2 ppm. Two thirds of these samples contained aluminium concentration less than 10 ppm. More than one quarter (26.7%) had aluminium concentrations between 10 and 50 ppm. Only 6.6% had greater than 50 ppm (Fig. 1). The market milk examined here revealed aluminium concentrations between 1.07 and

Table 1: Concentrations of aluminium (ppm) in milk and milk products samples

Products	No. of samples	Min.	Max.	Mean±SE
Farm milk	15	0.51	104.93	19.93±7.2
Market milk	15	1.07	270.63	107.32±26.9
Kareish cheese	20	1.40	251.38	52.36±1.70
Yoghurt	20	2.66	7.42	4.19±0.34
Rice pudding	15	1.70	361.36	80.97±2.60

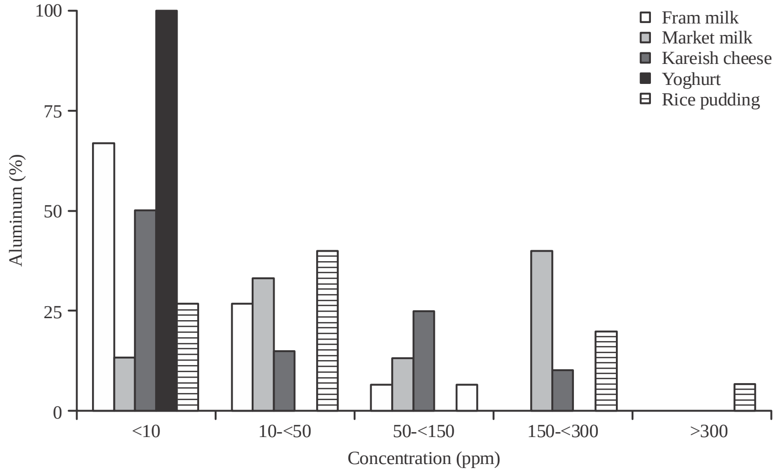

Fig. 1: Frequency distribution of aluminium levels in milk and milk products

270.63 ppm, with a mean value of 107.32±26.9 ppm. One third of these samples contained aluminium concentrations between 10 and <50 ppm. Forty percent had aluminium concentrations between 150 and <300 ppm (Fig. 1).

Many reports dealing with the aluminium contamination level in raw milk have been accumulated. In those studies, aluminium levels were reported as 3.76, 1.18, 7.427, 0.84, 0.37 and 0.501 ppm by Guler (2007), Birghila *et al.* (2008), Ayar *et al.* (2009), El-Mossalami and Noseir (2009), Gonzalez-Weller *et al.* (2010) and Abd-El Aal *et al.* (2012), respectively. Al-Ashmawy (2011) reported aluminium levels of bulk farm milk and market milk at 0.004 and 0.081 ppm, respectively. Aluminium concentrations measured in the market milk were significantly higher ($p \leq 0.05$) than those found in the farm milk (Table 1). A similar observation was reported by Al-Ashmawy (2011). In the present study, the aluminium levels obtained turned out to be higher than the reviewed studies. Large amounts of aluminium contamination can be resulted either from the abundant and traditional use of aluminium containers for production and storage of raw milk or by external environmental contamination during the phases of collection and transport of milk from the farms to the dairy shops.

Regarding kareish cheese, the aluminium contents were in the range of 1.4-251.38 ppm. Mean aluminium level was 52.36±1.7 ppm. Fifty percent of these samples contained aluminium concentration below 10 ppm. One quarter had aluminium concentrations between 50-<150 ppm (Fig. 1). The results obtained in the present study were higher than those obtained by Ayar *et al.* (2009) and Gonzalez-Weller *et al.* (2010) and lower than those reported by Deeb and Gomaa (2011) who determined a mean aluminium concentration of 57.58±3.44 mg kg^{-1} for kareish cheese.

Kareish cheese is one of the most popular types of soft cheese consumed in Egypt. The aluminium contents of kareish cheese were higher than those of the farm milk and lower than those of the market milk, but statistically not significant ($p \leq 0.05$) (Table 1). Aluminium contamination of kareish cheese can be resulted from the milk portion. This may be ascribed to the fact that the aluminium is preferentially bound to caseins and fat and consequently shift mostly to the curd. Also, a certain accumulation during the production process through aluminium utensils, salt and the environment can not, however, be excluded (Coni *et al.*, 1996). Additionally, the acidity of cheese can enhance corrosion of aluminium in pots and increases the rate of contamination with aluminium (Elbarbary and Hamouda, 2013).

Table 2: Intake of aluminium via consumption of milk and milk products

Products	Food intake	Average daily Al intake (mg day^{-1})	Average weekly Al intake (mg week^{-1})	PTWI (mg kg^{-1} b.wt.)	Contribution to PTWI (%)
Farm milk	0.2 L	3.99	27.902	0.470	23.25
Market milk	0.2 L	21.46	150.250	2.500	125.21
Kareish cheese	0.022 kg	1.15	8.060	0.130	6.72
Yoghurt	0.014 kg	0.06	0.410	0.007	0.35
Rice pudding	0.106 kg	8.60	60.100	1.001	50.10
Total		35.26	246.720	4.110	205.50

Table 3: Aluminium levels (ppm) in raw milk and milk products after processing in aluminium and stainless steel utensils

		Boiling			Kareish cheese			
Utensil	Raw milk	5 (min)	10 (min)	Yoghurt	Curd	Fresh	Whey	Storage at 4°C for 24 h
Aluminum	3.01	3.86	7.998	4.72	6.76	7.75	7.21	8.93
Stainless steel		2.98	3.380	3.15	3.51	4.97	6.31	3.61

In yoghurt, aluminium levels ranged from 2.66 to 7.42 ppm. All yoghurt samples had aluminium concentrations below 10 ppm (Fig. 1). These values were higher than those reported by Lopez *et al.* (2000) and Gonzalez-Weller *et al.* (2010) and lower than those reported by Ayar *et al.* (2009). Aluminium levels were significantly lower ($p \leq 0.05$) in yoghurt than in market milk and rice pudding (Table 1). Lower aluminium levels in yoghurt may be attributed to the fact that the yoghurt is fermented and stored in plastic containers.

Rice pudding is a product made of whole milk, rice, sugar and starch. The aluminium content of rice pudding ranged from 1.7 to 361.36 ppm, the mean value was 80.97±2.6 ppm. More than one quarter of these samples contained aluminium concentrations below 10 ppm. Forty percent of the samples had aluminium concentrations between 10 and <50 ppm. One sample had an aluminium concentration of 361.36 ppm (Fig. 1). In general, the aluminium contents of rice pudding were higher than those of farm milk, kareish cheese and yoghurt. Considering the aluminium levels found in milk, the determined aluminium values in rice pudding can be attributed to the milk portion. Contamination caused by rice, sugar, starch and processing equipment can not, however, be excluded.

Since aluminium is ubiquitous in the environment and is used in a variety of products and processes, daily exposure of the population to aluminium is inevitable (Soni *et al.*, 2001). Recently, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) established a Provisional Tolerable Weekly Intake (PTWI) of 2 mg kg^{-1} b.wt. (FAO/WHO., 2011) which means that for an average 60 kg person, a daily intake of 17.14 mg of aluminium is tolerable. In the present study, the aluminium daily intakes from farm milk, market milk, kareish cheese, yoghurt and rice pudding were 3.99, 21.46, 1.15, 0.06 and 8.6 mg day^{-1}, respectively. These values are equivalent to 23.25, 125.21, 6.72, 0.35 and 50.1% of the PTWI (Table 2). The biggest contribution to the intake of aluminium came from market milk and rice pudding, whereas, yoghurt contributed the least. The estimated total intake of aluminium via consumption of milk and milk products was calculated to be 246.72 mg week^{-1} which corresponds to 205.5% of the PTWI (Table 2). The increased aluminium consumption above the recommended PTWI may become a threat to humanity.

Humans are frequently exposed to aluminium. One of the potential sources of additional dietary aluminium is the aluminium utensils (Semwal *et al.*, 2006). The concentrations of aluminium in milk and milk products after processing in aluminium and stainless steel utensils are presented in Table 3. Aluminium level in milk boiled for 10 min in aluminium cookware was approximately twice higher than that of the raw milk, whereas, leaching of aluminium during boiling in stainless steel cookware was found to be negligible. Regarding yoghurt production, aluminium level in yoghurt manufactured in aluminium cookware was 1.5 fold higher than that manufactured in stainless steel cookware. Aluminium level in the kareish cheese processed in aluminium cookware was twice higher than that processed in stainless steel cookware. It was observed that the nature of the food has a great effect on the extent of aluminium leaching from the containers. High acidity products such as cheese and yoghurt resulted in greater leaching of aluminium into the food from the utensils. Similar observation has also been reported by Semwal *et al.* (2006). It was also observed that curdling gives rise to increased concentrations of aluminium in the curd and end product compared to raw milk. Similar observation has also been reported by Coni *et al.* (1996). In contrary, Elbarbary and Hamouda (2013) reported that the aluminium level decreases from 0.561 mg kg^{-1} in raw milk to 0.401 mg kg^{-1} in fresh cheese. It was also observed that the duration of heat treatment has a great effect on the aluminium leaching from the utensils. Furthermore, the results obtained suggest that leaching of aluminium was higher from aluminium than stainless steel utensils, indicating the advantage of using stainless steel utensils for heating, processing and storage of milk and milk products, especially those acidic in nature such as yoghurt and cheese.

CONCLUSION

The results clearly indicated that milk and milk products in Beni-Suef governorate are significantly contaminated with aluminium which may carry high health hazards to the consumers. Market milk, rice pudding and farm milk contribute greatly to the total weekly intake of aluminium than yoghurt and kareish cheese. With respect to the leaching of aluminium, the results indicated that processing and storage of milk in aluminium utensils raise aluminium content, so the use of such utensil is not recommended for processing and storage of milk products, especially those acidic in nature such as yoghurt and cheese.

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THE CORROSION OF METALS BY MILK

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INTRODUCTION

Milk is the most important food for human consumption. According to Holm (1) there was produced in the United States in 1926 53,000,000 tons of milk with a market value of about $4,000,000,000. By way of comparison, the value of the automobile industry is placed at about $3,500,000,000 and steel at $3,000,000,000.

Cooperative milk depots, pasteurizing plants and commerce have ordained the use of large installations of metal equipment. A very large proportion of the milk produced in America today is pasteurized in metal equipment.

In strong contrast to its very mild action on the organs of the human body, the effect of milk on most metals is quite pronounced, in fact, the corrosion of metals by milk is one of the most serious corrosion problems facing modern civilization and industry.

IMPORTANCE OF THE MILK CORROSION PROBLEM

Not only does the corrosion of metals by milk become an economic problem from the point of view of equipment replacement, but it is important also from the marketability and physiological factors involved. Improper equipment may lead to contamination of the milk by the products of corrosion to such an extent that not only is the flavor affected, but also the food value. The flavor may be affected by simple metal contamination, giving the characteristic metallic taste, or by the indirect action of the dissolved metals on the microorganisms in the milk, resulting in the "mealy" flavor (2).

A considerable amount of information has been obtained on the effect of metals in foods upon animals and human beings. The present paper is not intended to be a physiological treatment of the subject. However, this much can be said—nature has given us in milk a food which has been unchanged over thousands of years; it is hardly to be expected, in spite of many recent investigations indicating the contrary for iron and copper, that the addition of foreign metals in solution in the milk, as products of corrosion of equipment, will improve this food. Does it not seem logical that a milk which has been pasteurized in the proper metal equipment and has retained its original metal and other constituents without the intro-

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duction of foreign materials will be superior to a milk which has been relieved of part of its metallic contents or has been contaminated by foreign metals?

PREVIOUS INVESTIGATIONS

The corrosive action of milk on metals is by no means a new observation. It has long been known that milk in contact with iron and copper will not only acquire a metallic taste, but corrode these metals readily.

Supplee and Bellis (3) found that just a few bronze joints and tees in a pasteurizing unit would increase the copper content of the milk. The action of milk upon copper and other metals has been studied by Donauer (4), Rice and Miscall (5), Quam, Soloman and Hellwig (6), Miscall, Cavanaugh and Carodemus (7).

Nickel and Monel metal have been studied by McKay, Fraser and Searle (8), Flowers (9), and others. Chiara (10) studied these metals along with their zinc alloys.

Hunziker, Cordes and Nissen (11) have made a very extensive study of the action of milk upon a series of metals and alloys. These investigators and others have tested copper, nickel, aluminum, iron, tin, zinc, Monel (nickel-copper-iron alloy), German or nickel silver alloys, "stainless" alloys, etc.

METHODS OF INVESTIGATION

Almost all of the investigators determined the corrosion of the metals in milk by subjecting weighed samples of the metals to the action of milk for definite periods of time at certain temperatures. After the exposure the metal sample would be weighed again and the amount of corrosion estimated from the loss in weight. As will be shown later and has previously been pointed out by students of corrosion, loss in weight is not always a good criterion of the degree of corrosion. The accuracy of a loss-in-weight determination can, however, be greatly improved upon by visual or microscopic observations.

Almost all of the earlier investigators were unanimous in attributing the corrosion of metals by milk to acid corrosion, that is, substitution of hydrogen for metal.

STATUS OF METALS IN MILK EQUIPMENT

Hunziker, Cordes and Nissen (11), as a result of their recent detailed investigation, align the metals they tested into the following four groups, according to relative merit:

1. Allegheny Metal, tin, and heavily tinned copper.
   These metals have no effect on flavor and show maximum resistance to corrosion and tarnishing. The tin coating on copper must be heavy and intact.

2. Nickel, aluminum, and manganese aluminum alloy.
   These metals are not entirely satisfactory in high acid milk products. Furthermore, the nickel tarnishes readily and the aluminum is sensitive to alkali washing powders.
3. Monel Metal, Enduro, Ascoloy, and nickel silver.
   Monel Metal tarnishes appreciably in milk products. In these tests it had only slight effect on flavor. Enduro and Ascoloy are sensitive to high-acid products and their performance in dairy equipment is uncertain. Nickel silver tarnishes severely and was injurious to flavor in the majority of milk products.
4. Tinned iron, copper, galvanized iron, iron, and zinc.
   With the exception of properly tinned iron, this group is unfit for use in contact with milk products. Tinned iron is equally so whenever iron is exposed.

The above tabulation is not strictly in accordance with our own findings, notably in the case of the 18–8 chrome-nickel iron alloys. We group the metals and alloys as follows (see table, page 18):

(1) 18–8 alloys: (Allegheny metal, Enduro KA_2, etc.) Hyblum, tin, heavily tinned copper and chromium plated copper or nickel.
(2) 95 Copper–5 Nickel alloy, 12–13% chrome-irons.
(3) Monel, nickel-silvers, nickel, copper, aluminum, manganese, silicon-copper alloy, Ambrac.
(4) Iron, tinned iron, galvanized iron, zinc.

The basis for our tabulation will be evident from the experiments recorded in the following pages.

THE NATURE OF CORROSION

Before discussing the nature of corrosion by milk, it seems logical that one should first understand the fundamentals of corrosion by simple solutions. The electrochemical theory of corrosion is today almost universally accepted. When a metal goes into solution one can say then that it is the result of an electrochemical action. As the metal goes into solution and passes from a zero charge, as the metallic state is designated, to positively charged ions, an equivalent amount of electricity must pass from the solution to the metal so as to neutralize the charge. In the case of acid corrosion this may be expressed as follows:

$$M^{o} + H^{+}Cl^{-} \longrightarrow H^{o} + M^{+}Cl^{-} \qquad (1)$$

In the case of corrosion by metallic salts this may be expressed as follows:

$$M^{o} + Cu^{++}SO_4^{=} \longrightarrow Cu^{o} + M^{++}SO_4 \qquad (2a)$$

$$2\ M^{o} + Cu^{++}SO_4^{=} \longrightarrow Cu^{o} + M_2^{+}SO_4^{=} \qquad (2b)$$

In the case of corrosion due to the presence of oxygen, this may be expressed for copper as follows:

$$2\ \mathrm{Cu}\ (\text{metal}) + 2\ \mathrm{O} = 2\ \mathrm{CuO} \qquad (3a)$$

then

$$2\ \mathrm{CuO} + 2\ \mathrm{HCl} \rightarrow \mathrm{CuCl_2} + \mathrm{H_2O} \qquad (3b)$$

Before reactions 1 and 2 can proceed, the concentrations of acid and metallic salts must be high enough by Nernst's equation to make that reaction possible, thus at low concentrations of acid, or metallic salt, corrosion by these means may not be possible. Furthermore, in order that case (1) may be satisfied hydrogen must either evolve or be removed with oxygen, otherwise corrosion cannot proceed. This is the well-known phenomenon of over-voltage polarization and oxygen acts as a depolarizer.

The cases just presented are subjected to a number of factors which affect the speeds at which they proceed, such as chemical and physical conditions of the metal, kind of solvent, circulation, etc.

A point of note is that oxygen may sometimes, contrary to general belief, inhibit rather than assist corrosion. Thus, if the rate of oxygen supply permits the formation of slightly soluble oxide films, the metal is said to become passive and resists solution. This is frequently the case with iron and nickel, as investigated by Evans (12).

Every corrosion problem is a problem in itself, many times appearing to overthrow the fundamental concepts gained from other experiences. The problem of corrosion of metals by milk is one like this. Why milk should have such a profound effect on metals has never before been satisfactorily explained.

THE NATURE OF CORROSION BY MILK

Milk is known to be a complex body containing both organic and inorganic radicals. Ordinary milk tends to be slightly acidic, having a pH at room temperature of 6.6–6.7 when sweet, to 4.6 when sour. It is evident, then, that unless extreme precautions are taken immediately after the milk is drawn from the cow, it will become slightly acidic due to the lactic acid produced by bacteria (13). Increasing the temperature of milk increases the acidity (14), consequently this factor may be one of the explanations why the corrosion rate of metals in milk increases at the higher temperatures. Quam (15), as well as others, have found that the corroding action of milk on metals passed through a maximum at about 80°C., as the temperature of the milk was gradually increased.

It is quite evident that the acidity of milk is too low for Equation (1) to proceed in the absence of oxygen. That this is true can be ascertained from the results of Emery and Henley (16) who found that milk had very little effect on some metals in the absence of oxygen. As the temperature of milk is being increased, the oxygen content decreases, and the acidity, as mentioned before, increases and at the same time viscosity decreases (17). The first factor being unfavorable for corrosion above 80°C. must overshadow the favorable effects of viscosity and pH, causing a drop in the solubility rate curve. It is well known that above 80°C. the oxygen content of water, which may be compared to milk, decreases to almost zero.

The presence of a large amount of dissolved oxygen at the lower temperature might even act to inhibit the corrosion of such metals as nickel which readily forms protective oxide films. This may be one explanation why the average nickel pasteurizing unit does not corrode very readily in the cold sections of the equipment, yet frequently does corrode in the regenerator where a large amount of the oxygen is driven out of solution and leaves an insufficient amount to promote the formation of passive films.

Donauer (4) has calculated that the corrosion rate for most metals is ten times greater at pasteurizing temperature than at room temperature. That a certain amount of oxygen is necessary may be true for the type of corrosion as indicated by Equation (1), and, again, it is quite possible that an excess of oxygen will inhibit the corrosion of metals like nickel.

THE FINK THEORY OF CORROSION BY MILK

Fink attributed the corrosion of nickel by milk to the copper in the milk (18). It is the copper present in all normal milk that is responsible for a great deal of the observed corrosion. We may express the theory of base metals according to the Equation (2):

$$\mathrm{Ni} + \mathrm{Cu}^{++} \longrightarrow \mathrm{Ni}^{++} + \mathrm{Cu}$$

It is a well-known fact that all normal milk contains copper to the extent of 4–6 parts per ten million (19). This copper content is easily raised, as previously mentioned, by the presence of bronze, brass or copper fittings and equipment in contact with the milk. Moreover, the influence of oxygen is here very slight.

This type of corrosion, due to metal substitution, is similar to acid corrosion except that it is influenced by a greater potential, that is, in equimolecular concentrations of copper and hydrogen ions, nickel has a greater tendency, by about 0.3 volts, to go into solution in the presence of copper (20). This potential difference is, of course, influenced by the respective activity concentrations of hydrogen ions and copper, and may be mathematically expressed at 25°C. as:

$$\begin{aligned} E_1 &= \left(-.23 + \frac{0.059}{2} \log C_{\mathrm{Ni}}\right) - \left(+.34 + \frac{0.059}{2} \log C_{\mathrm{Cu}}\right) \\ E_2 &= \quad \text{``} \qquad\qquad \text{``} \qquad - (\;0 + 0.059 \log C_H) \end{aligned}$$

Subtracting,

$$E_3 = -.34 - \frac{0.059}{2} (\log C_{\mathrm{Cu}} - 2 \log C_H)$$

These equations demonstrate theoretically that the corrosion of nickel pasteurizing equipment is influenced more by the copper concentration of the milk than by the hydrogen-ion concentration. Moreover, hydrogen has a greater over-voltage than copper, making for an even greater difference. The argument may be advanced that the copper in milk is bound up into complex combinations and does not present the "activity" that the hydrogen ions do. That this argument is untenable will be shown later.

Rice and Miscall (5) have shown that, as milk was being handled in nickel cream separators, the copper content decreased. This decrease in copper could not have taken place without solution of nickel. A close examination of milk-shake mixers made of nickel will give evidence of a dark coloration that does not wash off. By taking a badly corroded nickel regenerator tube and dissolving this black coloration in nitric acid, we were able to electroplate copper out of the resulting solution.

LARGE SCALE TEST: CORROSION DUE TO COPPER

With this knowledge, and not disregarding the effects of acid corrosion and of oxygen, a test was made upon one of the pasteurizing plants of New York City. This plant was similar to the many other plants of the city; milk was stored in enamelled tanks, the pasteurizing equipment was constructed of nickel and copper with the usual bronze joints.

In this plant test samples of milk were taken from thirteen different locations or sections of the pasteurizing equipment. These samples were taken by a disinterested party and labelled by numbers, consequently, when they arrived in our hands, our only guide were the numbers. We had no information on any sample as to whether it had been in contact with either cold or hot metal or what this metal was.

DETERMINATION OF COPPER IN THE MILK SAMPLES

The samples of milk were then analyzed by the xanthate, colorimetric method. Many trial analyses on known water blanks containing organic matter were tried before the errors of the method were under control and the technique mastered. Duplicate samples of milk of 100 cc. each were slowly evaporated and ashed in 200 cc. silica evaporating dishes. The contents of the evaporating dish were protected from possible gas flame contamination by means of an asbestos collar.

Ashing in an electric furnace was tried but erratic results were obtained due to copper volatilization at the higher temperatures. Electric furnace ashing should no doubt be satisfactory if the temperature could be controlled within reasonable limits.

It was soon noted that the silica became covered with a dark crust which resisted later solution. This crust was found to dissolve in hydrofluoric acid. Consequently, after each ashing a few drops of hydrofluoric acid were added to the hydrochloric acid when the ash was to be dissolved. From here on the usual method was applied, namely, evaporation of the dissolving hydrochloric acid solution in water, addition of ammonia, filtration, and neutralization to the same pH. The identical quantities of water, acid, and ammonia were used with each milk sample and the analytical procedure, time, temperature, etc., were as nearly identical as possible. These preliminary steps were then followed by the colorimetric xanthate comparison with known standards. All comparisons were made in the same light and under the same conditions of temperature.

The above procedure in the copper determinations, although exceedingly laborious and requiring considerable care, gave very good checks and enabled us to predict whether the milk had gone over nickel or copper, or copper alloy. When it had passed over nickel, the copper content would decrease by reaction (2a), and when it had come into contact with copper, the copper content would increase by reaction (3). After completing the analyses a description of each sample of milk was furnished us, including temperature, metal contact, etc. In each one of the thirteen cases the amount of copper found agreed almost precisely with what was to be expected. We could thus tell in advance from the copper analyses whether the milk had just passed over copper or nickel metal. In one case only, where chromium plated copper equipment had come into contact with the milk, a very slight change was noticed which in due fairness could be attributed to a slight experimental error. A striking illustration of a series of tests was in the case of one of the regenerators. This regenerator was constructed as follows: The first six tubes were of pure nickel, followed by 8 copper tubes and then again by 16 nickel tubes. The analysis of the milk at the inlet of this regenerator indicated a copper content of 0.43 p.p.m. After passing through the six nickel tubes, the copper content dropped to 0.31 p.p.m. At the outlet of the eight copper tubes, the copper content was found to have increased to 0.76 p.p.m. At the outlet of the remaining tubes of nickel, the copper content of the milk was found to have dropped to 0.43 p.p.m.

These results are only examples of how the copper content varied in the entire pasteurizing equipment. A number of the nickel tubes exposed to the milk showed deeply corroded areas, indicating loss of nickel metal, and, although no analysis was made of the nickel content of the milk, it is safe to assume that the nickel content was accumulative because of the absence of any less noble metal for the nickel to plate out upon.

The copper analyses do, no doubt, vary from day to day, depending upon the rate of pasteurizing and temperatures, but will, we believe, always be in the same sensible order as found in this particular case.

DIFFERENCES IN CORROSION RATES

A careful corrosion study of a pasteurizing plant of this type revealed to us that the corrosion of the nickel is most severe in the regenerators. In almost all cases the most severe corrosion was found to have occurred in this portion of the equipment. Here the corrosion is so pronounced as to deeply pit the tubes. The nickel equipment in the other sections of the plant is not corroded to the same extent as the regenerator tubes.

A THEORY OF THE DEGREE OF CORROSION

As previously mentioned, in the presence of oxygen nickel has a tendency to form a protective film of oxide which resists corrosive action. Brown, Roetheli and Forrest (21) have recently made some very interesting measurements on the initial corrosion rates of several metals among which were nickel and copper. The results they obtained showed that in the presence of aerated water nickel went into solution much more slowly than copper. In other words, the oxide film that must first form in the case of nickel is less soluble and protects the underlying metal better than the copper oxide film. It must be remembered that in the presence of oxygen the potential of the metal is in reality the potential of the metal oxide. Too liberal a use of the electromotive series is then not permissible.

As these effects of oxygen and oxide films in water are no doubt approximately the same in the case of metals in milk, many apparent discrepancies can be explained. At first the milk is cold and contains a liberal amount of oxygen; then, as it passes through nickel equipment, very little action takes place—in fact, if a few copper tees and pipes are present, the copper content will quite likely increase instead of decrease. This was found by Supplee and Bellis (19) and confirmed by our own experiments. As this milk is fresh, the pH is high, generally around 6.6–6.7; consequently, acid corrosion is insignificant.

After the milk is heated to the pasteurizing temperatures and transported through pipes to the regenerators, a change in the milk takes place. As previously mentioned, the viscosity decreases and the pH decreases with a higher temperature. Above all, the amount of oxygen dissolved in the milk is decreased considerably: Consequently, nickel does not readily form a protective film in the presence of the low oxygen concentration. When the oxygen content of the milk drops below a certain value, the corrosion of the nickel increases, the rate for the formation of a continuous, protective film now being far below the corrosion or pitting rate. At the same time as the oxygen or air in the milk is eliminated, any copper that is present in the milk has a tendency to pass from the cupric (Cu^{++}) to the cuprous (Cu^{+}) state (22). Increasing the temperature also favors this tendency. When copper is in the cuprous state it has a greater tendency to plate out of solution because $Cu^{+} \rightarrow Cu^{0} - 0.51$ volts; therefore, in a heated solution of copper, or in heated copper containing milk, in the presence of a less noble metal like nickel, a greater corrosion rate, by metal substitution, will result than in the cold solution.

THE MECHANISM OF THE DISPLACEMENT REACTION

The action in the case of milk upon a metal like nickel may be visualized as follows: To begin with, a small amount of nickel goes into solution and at the same time copper metal plates out of solution. A couple is then formed on the surface of the nickel and more nickel goes into solution, resulting in a small pit on the surface of the tube. This may be called the primary stage of the corrosion.

In the second stage of corrosion another factor may enter in. Bacteria called thermophiles (23) are present in most milk, and, although physiologically harmless, thrive at high milk temperatures, and decompose the lactose to lactic acid. These thermophilic bacteria, or spore formers, are aerobic (oxygen consumers) and ''delight in living in the milk solids that might cook to the sides of the pasteurizing equipment'' (24). These bacteria have a tendency to seek the crevices of the tubes and resist all but the most thorough efforts of cleansing.

It is quite evident, then, that these bacteria will settle in the pits formed by the first stages of corrosion. After they have accumulated and multiplied, each pit will be an active corrosion center. The oxygen content of the pit will decrease, the acid concentration increase, and nickel will go into solution. This might be called the second stage of the corrosion.

The actual plant observations show that when the regenerator tubes are made of nickel they are badly pitted.

It is of interest to note that the interior of these tubes is dark in color. To test for the presence of copper deposited on the nickel, the inside of a tube section was swished with nitric acid. The tube brightened and the resulting solution was electroanalyzed. Immediately a copper deposit formed on the platinum cathode, thus proving that the dark colored deposit on the nickel tube wall was partly, if not completely, due to copper.

MILK CORROSION TESTS WITH OTHER METALS

In order to find a metal or alloy which would resist the corrosion of milk at low and high temperatures and which would be more suitable for pasteurizing equipment than any metal now in use, a new series of experiments was initiated. Small samples of metals and alloys were subjected to raw milk for definite lengths of time and at controlled temperatures. The milk was analyzed for copper before and after the experiment. Besides this, no other test except a visual examination was given each metal specimen after an experiment.

On the basis of the findings recorded above, it is obvious that, as a metal is being substituted for copper, the weight loss or gain will give very little information or indication as to the corrosion performance. On the other hand, an analysis of the solution or milk will certainly tell the story of the corrosion.

Inasmuch as copper has a very great tendency to go into solution in the presence of oxygen, and nickel has a tendency to displace copper from solution, it was thought that some alloy of the two metals might be made in which the tendency of one metal would counteract that of the other. We were encouraged in this belief since we had observed that nickel-copper alloys high in copper would, at any well defined temperature of the milk, lose copper, and alloys of the two metals high in nickel lose nickel. Accordingly, there ought to be an alloy of the two metals which at, say, pasteurizing temperatures would satisfactorily resist the corrosion by milk. The value of such an alloy is evident: corrosion would be eliminated and the copper content of the milk would remain undisturbed. Since Monel metal (approximately 28% Copper and 69% Nickel) is known to be corroded by milk, resulting in a milk high in copper, alloys of 5, 10, 15 and 20 per cent copper, balance nickel, were made up. These alloys were carefully made, poured into clean molds, given the same uniform heat treatment, and carefully polished.

Of this polished area 50 sq. cm. was then exposed to 200 cc. of raw milk at 40°F. (4.4°C.) for 60 hours. The raw milk previous to exposure showed copper to the extent of 0.50 p.p.m. The results of the analysis are as follows:

TABLE 1

COMP. OF CU-NI ALLOY		TIME OF EXPOSURE	TEMP. °F.	CU CONTENT OF MILK	
% Cu	% Ni	Hrs.		Initial	Final
				p. p. m.	*p. p. m.*
20	80	60	40	0.5	1.25
15	85	60	40	"	1.02
10	90	60	40	"	0.65
5	95	60	40	"	0.52
0	pure nickel	60	40	"	0.10

The metal specimens were all tarnished to about the same degree. It was quite evident, after the samples had been cleaned and then exposed to hot milk and had given the same trend in results, that no alloy of nickel and copper could be successfully employed at both temperatures to resist corrosive action of milk. The alloy of 5% Cu and 95% Ni did maintain a good copper balance in the milk at 40°, but not at higher temperatures.

All of the samples showed the characteristic discoloration due to the cementation of copper. It might seem peculiar that copper will plate out and/or go into solution from the same specimen. We may attribute this to a specific local action. When nickel and copper are melted together they form a simple, solid solution. Upon solidification, then, both nickel and copper will be in the space lattice. The copper in the milk will then substitute for the nickel in the alloy's surface. The result is a specimen presenting only a copper surface. As the concentration of oxygen builds up, the oxygen-liquid corrosion is now diverted to the copper, causing its solution, which results in nickel being uncovered and subjected to the attack. This cycle continues, and, as in the case of Monel metal, solution rate is faster than ordinarily.

OTHER ALLOYS INVESTIGATED

Allegheny metals, Nirusta, and other 18–8 alloys suggested themselves as possible substitutes for copper-nickel equipment. The results of the corrosion tests on these chrome alloys are given in table 2.

Alloys of nickel, copper and zinc have been recommended frequently for milk pasteurizing equipment. Recently the alloys Ambrac A and Ambrac B have been favored in some installations. These were tested by us and found to go into solution, bringing up the copper content, but leaving a smooth surface rather than a pitted surface. The results of these alloys, when corroded by milk, are also included in table 2.

The last alloy of promise that was studied in the research so far carried out was Hyblum. Hyblum is a high-aluminum nickel-aluminum alloy. It is very white, and light in weight. As the results in table 2 show, it gives promise of being good metal to use. However, it does not stand up well under the action of cleaning compounds that are commonly used in dairies.

TABLE 2

METAL	APPROXIMATE COMP. OR KIND	TIME OF EXPOSURE	TEMP. °F.	CU CONTENT OF MILK	
		Hrs.		Initial	Final
				p.p.m.	p.p.m.
Ambrac A	Cu 75, Zn 5, Ni 20%	24	145	0.55	2.05
Ambrac B	Cu 65, Zn 5, Ni 30%	24	145	0.55	1.15
Monel	30 Ni 70%	24	145	0.55	0.83
Nickel	Pure, rolled plate	24	145	0.55	>0.10
Hyblum	Al 95 Ni 5	60	40	0.50	0.50
Enduro KA_2	Ni 8, Cr 18, Fe 74	24	145	0.55	0.55
Allegheny	" " "	24	145	0.55	0.50

SUMMARY AND CONCLUSIONS

Investigators in the past have shown that:

(1) Copper, naturally present in small amounts in milk and other foods, is a physiologically necessary and important constituent (25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35).

(2) The natural copper content of milk varies between 0.3 and 0.7 parts per million.

Our own experiments demonstrate conclusively that:

(3) Copper, nickel and copper-nickel alloys, when exposed to milk during pasteurization, may bring about an increase above 0.7 p.p.m. or a decrease below 0.3 p.p.m. in the copper content of the milk.

(4) This change in the copper content of the milk is more pronounced at elevated temperatures.

(5) When milk in contact with nickel apparatus loses copper, this metal is precipitated out and nickel goes into solution.

(6) Nickel corrodes in milk more readily in the *absence* of oxygen.

(7) Copper corrodes in milk more readily in the *presence* of oxygen.

(8) High chromium nickel (18–8) iron alloys, "Hyblum," chromium-plated copper and chromium plated nickel are very resistant to corrosion by milk and are satisfactory for dairy equipment on this account.

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