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Study of the Changes in Cheese Making Parameters of Skim Milk with Divalent Cations Addition

Javier Solorza-Feria

CeProBi - IPN (Center of Development of Biotic Products),
Apdo. Postal 24, Yautepec, Morelos, 62730, Mexico

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Summary

The research was done in order to evaluate the effect of divalent cations (Ca^{2+} and Cd^{2+}) on the cheese making parameters of skim milk, during the manufacture of a model soft cheese. Four different concentrations of both cations (0.14, 0.35, 0.88 and 2.2 mM) were added to reconstituted skim milk with 9 % (w/v) total solids, to prepare a soft »stretchable« cheese of the Mozzarella type. Both minerals increased the ionic calcium concentration in milk and whey and also influenced most of the measured cheese making parameters (decreased clotting time, increased weight of whey and improved protein recovery) and showed increasing effects at higher ion concentrations. However, the addition of either mineral did not improve the corrected and dry weight yield of the treated samples.

The presented cheese making parameters showed that the effects of these chemically similar divalent cations were very similar.

Key words: stretchable cheese, Ca^{2+} and Cd^{2+} addition, cheese making parameters

Introduction

The exact mechanism behind the effect of Ca^{2+} and similar ions on the renneting process and subsequent steps during milk coagulation and cheese making has not yet been fully elucidated. As it was observed, multivalent cations had an effect on renneting, comparable to that of divalent cations. It suggests that the complexes may in fact also be positively charged, as it is in the case of micellar calcium phosphate (MCP) (*1,2*). The differences in composition of the complexes may determine their charge density and thereby, their effect on the renneting process. After renneting, the positive clusters presumably become exposed and enhance the interaction between micelles. From previous experiments with various types of cationic additives, it has been concluded that the casein aggregation was accelerated by the adsorbed cations, shielding the negatively charged groups of the casein. It has also been suggested that adsorption of cations would increase the hydrophobicity of the rennet-converted micelles, and therefore promote aggregation (*3*). There is also the possibility that renneting time may depend to some extent on the concentration of trace metals in milk since the addition of small amounts of some heavy metal salts (*e.g.* Mn^{2+}, Cd^{2+}, Zn^{2+}) shortens renneting time while the addition of others (*e.g.* Co^{+}, Cu^{+}, Ni^{+}) lenghtens it (*4*).

The expression of cheese yield is important in the economic control of cheese making and in expressing results of cheese making experiments. Yield of cheese is obviously important in the profitability of a cheese plant. The essential statistic is the cost of milk/Kg of cheese. The economic drive is to keep the cost of that milk as low as possible by improving yield (*5*). Payment

* Corresponding author; Phone: ++52 739 42020; Fax: ++52 739 41896; E-mail: jsolorzaferia@hotmail.com, jsolorza@redipn.ipn.mx

on the basis of fat and protein brings most milk samples to a common cost of milk for cheese, particularly milk samples standardized to a constant ratio of casein to fat. It is recommended that actual yield be compared with the theoretical yield to estimate yield efficiency (*5*).

The objective of this study was to evaluate the effect of the addition of cations with the same charge and similar ionic radius (Ca^{2+} and Cd^{2+}) to skim milk on the cheese making parameters during the manufacture of a model mexican soft cheese, and hence assess the ion specificity of calcium.

Materials and Methods

Starter cultures

Freeze-dried (DRI-VAC) type of starter cultures for traditional propagation were supplied by Christian Hansen's Laboratories, Copenhagen, Denmark. They were identified as thermophilic cultures of lactic acid bacteria: *Streptococcus thermophilus (S. thermophilus* CH-1), and *Lactobacillus delbrueckii* ssp. *bulgaricus (L. bulgaricus* CH-2).

Cheese making

Standard Cheese Rennet from Christian Hansen's Laboratories, Reading, U.K. was used. Skim milk powder was supplied by Kerrygold (Irish Dairy Board), this was used to prepare 1 litre volumes of reconstituted milk with 9 % (w/v) total solids to which calcium chloride ($CaCl_2$) and cadmium chloride ($CdCl_2$) was added according to the batch, making a total of five levels of calcium and five levels of cadmium (0.0 or control, 0.14, 0.35, 0.88, 2.2 mM). All milk samples were prepared using deionised water. A stranded white soft cheese similar to Mozzarella, known by the names of »Asadero« and »Oaxaca« in Mexico, a local »stretchable cheese« higly consumed on the central part and south of the country, was prepared from each of the milk samples following a modified traditional method as described previously (*6*).

Sample analyses

Chemical analysis of the cheese samples included fat, protein, moisture, ash and total solids; using the standard techniques specified by Case *et al.* (*7*). The pH was measured with a digital pH meter, model EIL 7045/46 from Kent International Measurements, at 25 °C. To determine calcium and cadmium content in milk and cheese the method described by Kirk and Sawyer (*8*) was followed, using an atomic absorption spectrophotometer (Pye Unicam model SP9, Cambridge, U.K.). To determine phosphorus, a method using molybdenum-blue solution, as described by Tusl (*9*) was used. The clotting time of the milk samples was measured following a procedure described by Bakker *et al.* (*10*), a visual technique where the clotting time was considered as the time for the first clot of milk to appear on the walls of a test tube, after the rennet addition. To determine the actual casein content of the milk the technique of the International Dairy Federation (*11*) was used. The ionic calcium levels were determined in milk (pH ≈ 6.7) and whey (pH ≈ 5.5) using an Ion Selective Electrode, ISE Ca^{2+}/pH analyser (model 634, Ciba Corning Company Diagnostics Limited, Essex, U.K.). The cheese making parameters were obtained by applying the following formulae (*12*).

$$1.\ AY = \frac{\text{Weight of curd}}{\text{Weight of milk}} \times 100$$

$$2.\ \underset{(47\,\%\ \text{moisture})}{CY} = \frac{(\text{Weight of curd} \times 0.47)\ \text{kg water in 1 kg curd}}{\text{Weight of milk}} \times 100$$

$$3.\ DWY = \frac{\%\ \text{Total solids in curd} \times \text{Weight of curd}}{\%\ \text{Total solids in milk} \times \text{Weight of milk}} \times 100$$

$$4.\ PR\ (\%) = \frac{\text{Total nitrogen in cheese (\%)}}{\text{Casein nitrogen in milk (\%)}} \times CY$$

Note: AY=Actual Yield, CY=Corrected Yield, DWY=Dry Weight Yield, PR=Protein Recovery
Curd = Cheese, Weight = mass

Data analysis

A balance of calcium and phosphorus was done taking as a basis the weight of one liter of milk sample (density), and the weight (mass) of the cheese obtained, considering the mineral concentration both in milk and cheese as well.

Statistical analysis was carried out by applying Analysis of Variance (F test, ANOVA) at the level of significance α = 0.05, to the results of »yields« and protein recovery. When the F value of the ANOVA test was significant, the multiple comparison procedure of Tukey (α = 0.05) described by Montgomery (*13*) was applied to each of the two pairs of mean values to find real significant differences.

Results

The mineral composition of both milk and cheese, following the addition of calcium and cadmium is shown in Table 1. There was a gradual increase in the concentration of calcium in both the milk and the cheese, as the amount of added calcium increased. As expected, cadmium was detected in higher concentrations with corresponding increases in the treated milk samples. The ionic calcium also showed an increase in concentration in milk and whey as the levels of added calcium and cadmium increased. This »incremental« increase was larger for the two final calcium concentrations (0.88 and 2.2 mM, respectively). The ionic calcium values in milk increased between 31 and 36 %, as a result of the addition of the different levels of calcium. As the amount of added calcium increased, the concentration of phosphorus in the cheese also increased; the opposite effect was observed in milk and cheese for cadmium addition (Table 1).

The effect of the various calcium and cadmium levels on the clotting time and the weight of whey expelled during cheese making is shown in Table 2. There was a decrease in the clotting time (CT) of the milk as the calcium concentration increased. Cadmium addition up to

Table 1. Mineral composition of milk and cheese

SAMPLE	*w*(total Ca in milk)	*c*(Ca^{2+} in milk)	*c*(Ca^{2+} in whey)	*w*(total P in milk)	*w*(total Ca in cheese)	*w*(total P in cheese)
	%	mM	mM	%	%	%
CONTROL	0.112	1.91	2.36	0.084	0.65	0.59
0.14 mM Ca	0.1126	1.96	2.62	0.084	0.785	0.70
0.35 mM Ca	0.1134	2.03	3.07	0.084	0.867	0.757
0.88 mM Ca	0.1155	2.18	4.01	0.084	0.92	0.795
2.20 mM Ca	0.1208	2.58	6.6	0.084	0.942	0.806
	w(total Cd in milk)					
	%					
0.14 mM Cd	0.00016	1.91	2.59	0.082		0.419
0.35 mM Cd	0.00042	1.93	2.61	0.080		0.383
0.88 mM Cd	0.00104	2.07	3.01	0.079		0.326
2.20 mM Cd	0.0026	2.45	3.30	0.078		0.301

Maximum variation for the total calcium in milk was 3.2 % and in cheese 4 %; maximum variation for the total phosphorus in milk 2.6 % and in cheese 3 %; maximum variation for the ionic calcium in milk was 0.01 mM and in whey 0.02 mM (average values, N=4)

Table 2. Changes in clotting time and whey expulsion during cheese making

Milk sample	Clotting time[1]	Decrease in clotting time	*w*(Whey)[2]	Increase in whey expulsion
	min	%	g/kg milk	%
CONTROL	24.3	--	737.52	--
0.14 mM Ca	24.0	1.4	773.83	4.9
0.35 mM Ca	22.3	8.2	802.39	8.8
0.88 mM Ca	19.7	18.8	829.02	12.4
2.20 mM Ca	16.4	32.4	862.84	16.9
0.14 mM Cd	21.9	9.8	766.61	3.9
0.35 mM Cd	21.6	12.2	817.1	10.8
0.88 mM Cd	21.1	13.1	826.62	12.1
2.20 mM Cd	18.9	22.4	874.62	18.6

1, maximum variation in results observed for cloting time, 0.42 min
2, maximum variation observed for weight of whey, 9.32 g
(average values, N=4)

0.35 mM reduced the clotting time more than the equivalent calcium addition and further additions (0.88 and 2.2 mM) produced lesser effects than the equivalent calcium additions. The weights of whey expelled for the calcium treated samples were, however, similar to those of the cadmium treated samples (Table 2). Addition of the highest cadmium concentration produced a cheese which had a »crumbly« texture, unusual for this type of cheese.

The higher whey expulsion in the treated samples and a subsequent reduction in water retention produced the expected changes in cheese yield (Table 3). The weight of the cheese decreased as the concentration of the mineral added (calcium or cadmium) was increased. The »actual yield« and »corrected yield« also followed this same general trend (with the exception of the samples with 0.14 and 0.35 mM calcium addition which showed the same values for »corrected yield«). For calcium treated samples, decreased weights of the curd (as a result of a higher amount of water expulsion) produced increases in the »dry weight yield« (where the solids concentration is more important) up to a maximum at 0.35 mM, but further additions caused the opposite effect. For cadmium treated samples however just the last concentration caused a decrease in this »yield«. The »Yield« values of Ca^{2+} treated samples were higher than those of Cd^{2+} treated samples at equivalent concentrations.

Increasing additions of the two minerals (Ca^{2+}, Cd^{2+}) gave an increased recovery in total protein (Table 4), showing the maximum protein recovery for calcium treated samples at 0.35 mM addition, whereas for cadmium treated samples it was at 0.88 mM. However, it was noted that the calcium treated samples gave greater overall protein recovery than those observed for cadmium (96.6 and 88.8 % for 0.35 mM Ca^{2+} and Cd^{2+} addition, respectively).

The samples of cheese with the highest calcium concentrations added (0.88 mM and 2.2 mM) reached the desired pH (pH=5.5) in the shortest time (about 4.5 h) (Fig. 1) compared with the cadmium treated samples (10 to 12 h) (Fig. 2).

Table 3. Cheese yield values

Milk sample	Mass / g	»Actual yield«[1]	»Corrected yield«[2]	»Dry weight yield«[3]
CONTROL	96.15	9.5 a, c	7.3 e, f	42.9 g, h
0.14 mM Ca	93.05	9.2 a	7.4 e	43.8 g
0.35 mM Ca	90.27	8.9 a	7.4 e	44.5 g
0.88 mM Ca	85.46	8.4 b	7.2 e	43.4 g
2.20 mM Ca	83.78	8.3 b	7.0 e	42.3 g
0.14 mM Cd	91.72	9.1 c	7.0 f	41.1 h
0.35 mM Cd	87.57	8.6 c	7.0 f	41.7 h
0.88 mM Cd	86.56	8.5 c	7.0 f	41.6 h
2.2 mM Cd	81.72	8.1 d	6.6 f	39.5 h

[1], in kg cheese/100 kg milk (Partridge *et al.* (*12*)); [2], corrected for 47 % moisture (Partridge *et al.* (*12*)); [3], as % of dry weight (Partridge *et al.* (*12*)); maximum variation for the »yields« was 0.3; maximum variation for the cheese weight was 2.65 g. Figures with the same suffix did not show any significant difference at $\alpha = 0.05$ (Tukey multiple comparison), (average values, N=4)

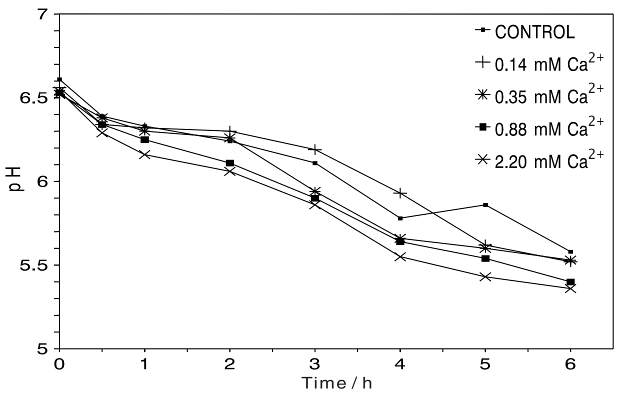

Fig. 1. Effect of four levels of calcium on the pH during the cheesemaking

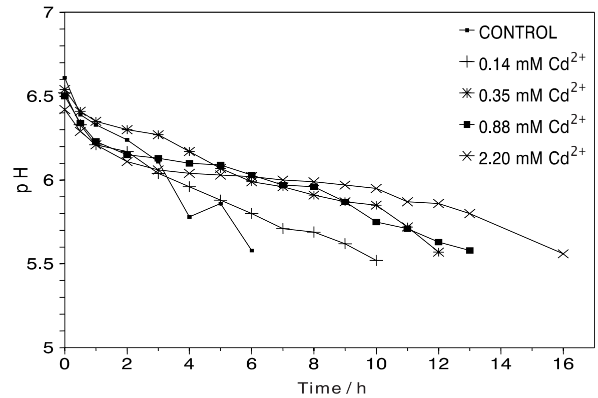

Fig. 2. Effect of four levels of cadmium on the pH during the cheesemaking

Discussion

The calcium and phosphorus composition of the cheeses produced with milk samples treated with Ca^{2+} were different than the »normal« ranges previously reported for such materials (ranges of 0.6–0.83 % and 0.44–0.55 % for calcium and phosphorus, respectively) (*14*) as is shown in Table 1, milk samples treated with Cd^{2+} gave as a result cheeses with decreased content of phosphorus.

This study has shown that content of calcium and phosphorus in cheese may be the result of the combination of intense heat treatment (cooking) and the low pH of the curd during manufacture, which induces whey expulsion and solubilisation of both minerals into the whey as suggested by Czulak *et al.* (*15*).

Ionic calcium levels in milk samples, such as those seen in this study (Table 1), have been previously reported (range: 1.4 to 2.5 mM) (*16*), and while they may be considered to be »low« in comparison with other experimental values (range: 2.5 to 3.4 mM) (*17*), this may be explained by the raw materials used in this study. All milk samples were reconstituted from spray-dried milk, a process which has been suggested to considerably reduce the ionic calcium content of the final product (reconstituted milk) (*18*).

The balance of the total calcium during the cheese making resulted in approx. 54 % calcium recovery in the cheese for the control, while those for calcium treated samples ranged between 63 and 67 % of calcium recovered (33 to 37 % lost in the whey, Table 4), This is consistent with the study of Kindstedt *et al.* (*19*), who reported average losses of calcium in the whey of 33.1 to 42 %. The balance of phosphorus gave a value of approx. 66 % recovery of this mineral in the cheese for the control, with a substantial increase for calcium treated samples (between about 75 to 81 % phosphorus recovery), while cadmium caused a decrease in phosphorus recovery (Table 4). This suggests that the added calcium is binding phosphorus, probably in the formation of colloidal calcium phosphate (*1*). This effect seems to be more pronounced than that of the pH, which would favour a higher expulsion of calcium than phosphorus as the pH decreases (*20*). While addition of calcium to the milk produced elevated levels in both the total calcium in the cheese and ionic calcium in the whey expelled from it, equivalent additions of cadmium

Table 4. Protein and minerals recovery during cheese making

Milk sample	*w*(casein N in milk) / %	*w*(total N in cheese) / %	Protein recovery[1] / %	P recovery / %	Ca recovery / %
CONTROL	0.412	4.88	86.5 a	65.99	54.53
0.14 mM Ca	0.412	5.28	94.8 b	75.50	63.16
0.35 mM Ca	0.412	5.39	96.8 b	79.20	67.19
0.88 mM Ca	0.412	5.45	95.2 b	78.75	66.28
2.20 mM Ca	0.412	5.49	93.3 b	80.60	63.61
0.14 mM Cd	0.412	5.13	87.2 a	45.63	–
0.35 mM Cd	0.412	5.24	89.03 a	40.82	–
0.88 mM Cd	0.412	5.31	90.2 a	34.77	–
2.20 mM Cd	0.412	5.46	87.2 a	30.71	–

[1], as described by Banks *et al.* (*27*); maximum standard deviation for protein recovery was 1.4 %; maximum standard deviation for phosphorus recovery was 2.7 %; maximum standard deviation for calcium recovery was 2.3 %. Figures with the same suffix did not show any significant difference at $\alpha = 0.05$ (Tukey multiple comparison), (average values, N=4)

Table 5. Chemical composition of the soft cheese

Cheese sample	Moisture fraction / %	*w*(total solids) / %	*w*(protein) / %	*w*(fat) / %	*w*(ash) / %
CONTROL	60.75	39.25	31.14	0.450	2.78
0.14 mM Ca	58.60	41.40	33.69	0.496	3.07
0.35 mM Ca	56.65	43.35	34.39	0.578	3.23
0.88 mM Ca	55.35	44.65	34.79	0.618	3.25
2.20 mM Ca	55.58	44.42	35.01	0.636	3.60
0.14 mM Cd	60.59	39.41	32.74	0.472	3.21
0.35 mM Cd	58.09	41.91	33.41	0.514	3.25
0.88 mM Cd	57.76	42.24	33.88	0.588	3.30
2.20 mM Cd	57.46	42.54	34.81	0.642	3.33

(average values, N=4)

produced a reduction in the ionic levels in the expelled whey (Table 1), despite the longer draining times employed.

The observed increases in the levels of ionic calcium in the whey (measured at its final pH ≈ 5.5) were expected, and this is probably due to the conversion of the colloidal calcium phosphate to ionic calcium. This is consistent with the theory that calcium binds to the casein micelles releasing protons in such a way as to reduce the repulsive forces between them, perhaps by promoting hydrophobic interactions, stimulating coagulation, curd firming and whey loss (*21*). The range of incremental values of the added calcium which appeared as ionic calcium in milk (about 31 to 36 %) was higher (Table 1) than the one mentioned by Demott (*16*), for approx. 21 %, but in agreement with those of Gastaldi *et al.* (*22*) and Brule and Fauquant (*23*). As expected, all of the added Ca^{2+} did not appear as free Ca^{2+} in the milk, suggesting that the milk solids still had a capacity to bind further ions either directly as Ca^{2+} or indirectly through salts of ester phosphate groups (*24*). Overall ranges found in this present study are within the ranges of those reported previously (1.4 to 2.5 mM) (*16*). Added cadmium produced an increase in the ionic Ca^{2+} both in milk and whey with no evidence of a »saturation level« being achieved. This is not an addition effect, but suggests that Cd^{2+} can displace Ca^{2+} from the protein system (Table 1).

Cadmium, similarly to calcium, produced decreasing clotting times with increasing concentration, with no significant ion specific effect (compare reductions on additions of different levels of ions, Table 2) in agreement with previous reports (*4*). However, major effects of cadmium were observed on the acidification profile when compared with Ca^{2+} (Fig. 2), suggesting that cadmium may well be inhibiting for the starter cultures with a consequent substantial reduction in the rate of acidification with increasing concentration. It is known that even at low concentrations cadmium acts on the sulfhydryl groups of essential enzymes and also binds to phospholipids and nucleic acids interfering with oxidative phosphorilation (*25*). The final cheese »yields« were again found to be related to the initial conditions of coagulum formation (Table 3). These values were relatively low compared to what would be expected, and may be due to protein losses in the whey during the cheese making (a loss of 3.8 % of protein nitrogen during cheese making due to rennet action has been suggested by Walstra and Jenness (*26*) which is less than what was actually lost in this process). The level of calcium addition chosen, however, did not produce drastic changes both in the corrected and dry weight yield of the »finished« material (cheese, Table 3). The protein recovery of the treated samples was better than that of the control (approx. 80–90 %, w/w, Table 4), but for cadmium treated samples it is still lower than would be found for a commercial operation (well above 90 %, w/w) (*27*). This »improved« protein recovery may be associated to the heat treatment of the milk samples; pasteurization had little effect on fat recovery in the cheese, but nitrogen recovery was improved, probably because of the association of the whey proteins with casein micelles after pasteurization (*28*). Further development work would be required to improve the model, however, recoveries were considered adequate for comparative purposes (Table 4). From the chemical composition of the cheeses made with both calcium and cadmium treated milk samples, it was observed that both the calcium and cadmium treated samples showed a decrease in overall moisture content in the final cheeses, with increasing added mineral levels (except for the 2.2 mM calcium sample, Table 5). Such changes have already been explained as a result of the greater whey expulsion for the mineral treated samples, as reflected in the final chemical composition of the cheeses made from such milk systems (Table 5) and were slightly lower than the ranges of values reported previously for this type of cheese (*29*).

The initial and final pH values (at 0 and 6 h) were lower for the higher concentrations of added calcium, however intermediate values did not always exhibit this trend (Figs. 1 and 2). The pH variation during the cheese making, at four levels of cadmium, showed differing profiles than those observed for calcium. The initial pH (time zero) was lower for the cadmium treated samples than for the control, but the time taken to reach the desired pH (pH=5.5) was substantially longer (12 h) for the higher cadmium concentrations (Fig. 2).

Substantial differences were observed in the time of the acidification profiles between samples with the last two levels of calcium and cadmium addition (cadmium treated samples lasted between 2 to 3 times compared to calcium treated samples, Figs. 1 and 2). This may suggest that there was some variation in the acid production caused by the different batches of the starter cultures.

Conclusions

The addition of both calcium and cadmium increased the ionic calcium concentration in milk and whey, suggesting a distribution of the added mineral in both a bound and soluble (ionic) form, with displacement of the calcium by cadmium in the system. The rennet clotting time was reduced as the concentration of the added minerals increased, with a greater effect noted for calcium only at higher concentration. Similarly, whey expulsion and a corresponding solids concentration were observed to increase as the mineral addition increased. The addition of calcium to the milk not only enhanced the retention of this mineral in the cheese, but also that of phosphorus. The addition of either mineral did not improve the »corrected yield« neither the »dry weight yield« of the treated samples. Protein recovery values were relatively lower than those expected, suggesting high losses of these components in the whey during the cheese making, which in turn affected the overall »yields«. The addition of more than 0.35 mM Cd^{2+} to the milk inhibited the acid development during cheese making, prolonging as a consequence the cheese making time. The presented results of manufacture of the model mexican cheese showed that the effects on the cheese making parameters of these chemically similar divalent cations were similar.

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Promjene parametara tijekom proizvodnje sira od obranog mlijeka uz dodatak dvovalentnih kationa

Sažetak

Provedena su ispitivanja da bi se utvrdio utjecaj dvovalentnih kationa (Ca^{2+}i Cd^{2+}) na parametre za proizvodnju mekoga sira od obranoga mlijeka. Četiri različite koncentracije obaju kationa (0,14, 0,35, 0,88 i 2,2 mM) dodavane su u rekonstituirano obrano mlijeko s 9 % ukupne suhe tvari kako bi se pripravio rastezljivi meki sir tipa Mozzarella. Oba kationa povećavala su koncentraciju iona kalcija u mlijeku i sirutki te znatno utjecala na izmjerene parametre tijekom proizvodnje sira (skraćeno vrijeme grušanja, povećana masa odvojene sirutke i poboljšano iskorištenje proteina), a pri većoj koncentraciji iona imali su pojačani utjecaj. Međutim, dodatkom bilo Ca ili Cd nije se poboljšalo iskorištenje korigirane i suhe tvari uzoraka. Praktički je isti utjecaj tih kemijski sličnih dvovalentnih kationa na promjene parametara tijekom proizvodnje sira.