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Polymeric Composite Materials Based On Silicate; I-Synthesis, Characterization And Formation Mechanism

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Abstract
Magneso-silicate has been synthesized by precipitation technique. Polyacrylamide acrylic acid and polyacrylamide acrylonitrile impregnated with inorganic ion exchanger, magneso-silicate,have beensynthesized by subjected co-monomers to gamma radiation initiated polymerization at radiation doses 25, 65 and 90KGy. The structure features of composites were investigated by sequential x-ray fluorescence spectrometer, x-ray diffraction, differential thermal- thermogravemetric analyses andinfrared spectroscopy.Formation mechanismfor these composites were conducted and the results obtained showed thatthe polymerization process were carried out in the hydrocarbon chain by addition polymerization whereas impregnation of magneso-silicate into the polymeric composites were carried out by condensation polymerization.

Keywords: *Magneso-Silicate, Co-Monomers, Gamma Radiation, Condensation Polymerization.*

1- INTRODUCTION

Now inorganic ion exchange materials play an important role in analytical chemistry, based originally on their resistance to chemical attack as well as their thermal and radiation resistance **[1,2]**. Polymers can be synthesized through various techniques such as radical, cationic and anionic polymerization**[3]**. The structural,mechanical and thermal properties can be investigated through different kinds of characterization methods to determination of structure property relationships**[3,4]**. Recently, polymers have been applied in various fields such as automotive, construction, electronic, cosmetic and pharmaceutical industries due to its advantageous material properties. Functional polymers ofphotochromic**[5]**, electrochromic**[6]** andoptoelectronic**[7]** functions were developed recently. The use ofpolymers with tunable refractive properties as opticalmodulators, optical filters, or electro optic waveguide deviceshas been reported**[8]**.The development of new inorganic ion exchangers with characteristic properties is still need attention and their utility in diverse fields is yet to be explored. Synthetic ion exchangers are used on a wide range for different applications, ranging from environmental remediation **[1,9,10]**, water softening **[10]**, hydrometallurgy **[10]** and selective adsorption **[11,12]** to medical applications **[13-15]**. Different materials based on silicate salts and poly acrylamide acrylic acid silicon titanate were synthesized earlier by Abou-Mesalam et al. **[1,11,16]** and used for removal of some heavy metals from industrial and hazardous waste solutions.

In this work magneso-silicate(MgSi) as inorganic ion exchange materialwas synthesized using precipitation technique. Polyacrylamide acrylic acidP(AM-AA), polyacrylamide acrylonitrileP(AM-AN), polyacrylamide acrylic acid magneso-silicate {P(AM-AA)-MgSi} and polyacrylamide acrylonitrile magneso-silicate {P(AM-AN)-MgSi} composites have been synthesized by gamma radiation initiated polymerization at radiation doses 25, 65 and 90KGy. The prepared compositematerials were analyzedby different analytical techniques and a new ion exchange character was represented compared to the original ones.

2- EXPERIMENTAL

All chemicals and reagents used were of analytical grade.

2.1- SYNTHESIS OF MAGNESO-SILICATE COMPOSITE

Magneso-silicate ion exchange material was synthesized as reported earlier by Abou-Mesalam et al. **[1,11,14]** by the addition of equimolar solutions (0.5M) of magnesium chloride to sodium metasilicate dropwisely with volumetric ratio for (Mg/Si) equal 1.5 with continuous stirring in a water bath adjusted at 60±1°C. The mixed solutions were immediately hydrolyzed in demineralized water. Diluted ammonia solution was added to the mixture until complete precipitation attained. The precipitate formed was kept in the mother solution to overnight standing. The precipitate was washed several times with distilled water, and then washed by 0.1M HNO_3 to remove impurities and Cl^-ions. The precipitate rewashed by distilled water to remove NO_3^-ions. After drying at 60±1°C, solid was poured in near boiling distilled water heated at 70±1°C to break the solid and remove air trapped inside the solid, then redried at 60±1°C. The obtained solid was ground and store at room temperature.

2.2- SYNTHESIS OF MONOMER SOLUTIONS

The investigated monomer solutions, acrylamide (AM), acrylic acid (AA) and acrylonitrile (AN) were prepared by dissolving 10% of each monomer in deoxygenated water.

2.3- SYNTHESIS OF CO-MONOMER SOLUTIONS

The acrylamide (AM) monomer solution was mixed with an aqueous solutions of acrylic acid (AA) and acrylonitrile (AN) by dropwith addition at constant stirring and room temperature with volumetric ratio equal unity for the preparation of (AM+AA) and (AM+AN) co-monomers, respectively. Then the (AM+AA) and (AM+AN) co-monomers were mixed with equimolar solutions (0.5M) of sodium metasilicate and magnesium chloride hexahydrate by dropwith addition at constant stirring and room temperature with volumetric ratio (AM-AA-Mg-Si) and (AM-AN-Mg-Si) equal 1:1:1.5:1, respectively.

2.4- SYNTHESIS OF P(AM-AA), P(AM-AN), {P(AM-AA)-MGSI} AND {P(AM-AN)-MGSI} COMPOSITES

P(AM-AA), P(AM-AN), {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites were prepared by subjected mixtures of (AM+AA), (AM+AN), (AM+AA+Mg+Si) and (AM+AN+Mg+Si) co-monomers to gamma radiation at radiation doses 25, 65 and 90KGy with dose rate 1.05KGy/h. After irradiation, the obtained hydrogel was cut into small pieces with a stainless steel scissors, soaked in acetone for removal of unreacted monomers, washed with water**[17],**dried at 50°C, grained, sieved for different mesh sizes and stored at room temperature**[18].**

2.5- COMPOSITION AND CHARACTERIZATION OF SYNTHESIZED COMPOSITES

IR spectra of MgSi,P(AM-AA), P(AM-AN), {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} compositesprepared at different radiation doses were carried out by mixing of the solid with KOH in ratio 1:5 and ground to a very fine powder. A transparent disc was formed in a moisture free atmosphere. The IR spectra were recorded using BOMEM FTIR spectrometer in the range 400–4000 cm^{-1}.

The stoichiometry of the constituents in MgSi and polymericcomposites based tosilicate prepared at different radiation doseswere determined using Philips sequential x-ray spectrometer-2400. The solid samples were ground to very fine powders and then mixed with H_3BO_3 as a binder to facilitate the pressing process. The mixture was pressed in a sample holder of 40mm diameter aluminum cups and pressed on pressing machine at 20 psi to produce a sample with the diameter of 40mm and 5 mm thickness. The concentrations of magnesium and silicone were measured according to Super-Q quantitative application program.

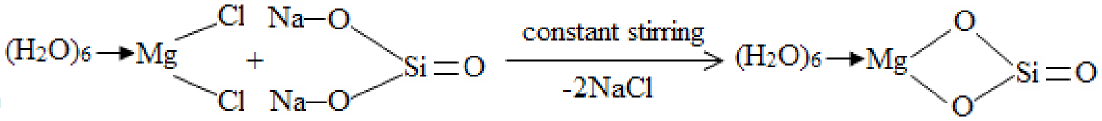
X-ray diffraction patterns of prepared composites were carried out using a Shimadzu XD-D1, X-ray diffractometer with Cu-K_α radiation tube source (λ=1.5406A°) and graphite monochromator operating at 30kV and 30mA. The measurements were done in 2θ ranges from 4 to 90 with scan speed 2°/min.

Prepared composites (20mg) were analyzed for DTA and TGA with sample holder made of Pt in N_2 atmosphere using a Shimadzu DTG-60H. The heating rate was maintained at 10°C/min with using alumina powder as reference material.

3- RESULTS AND DISCUSSION

The scope of this study is the attempt to synthesize a high chemical stable inorganic, organic and composite ion exchange materials with high selectivity for some heavy metals. MgSi, P(AM-AA), P(AM-AN), {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites prepared at different radiation doses have been synthesized with complete characterization for ion exchange materials.

Magneso-silicate (MgSi) was prepared earlier in our laboratories by Abou-Mesalam et al.**[11]**.The formation mechanism of prepared MgSican be represented as shown inscheme (1).Magneso-silicate material was obtained by substitution of two Na$^+$ions by one Mg^{2+}ion and elimination of two molecules of NaCl.

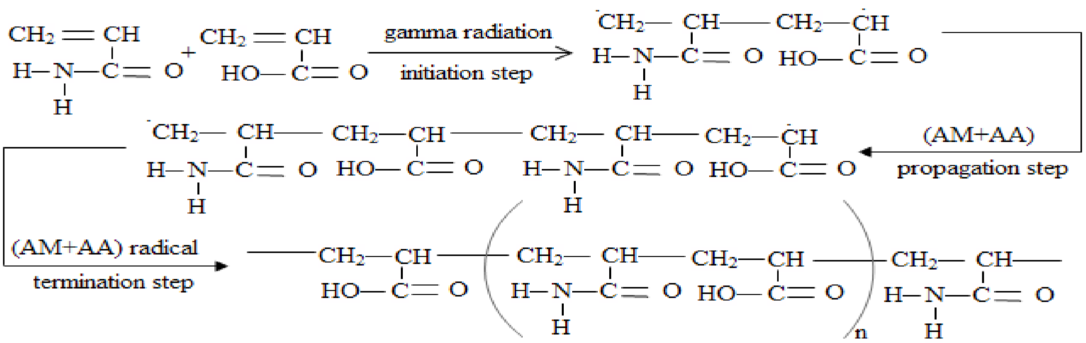


Scheme (1): Formation mechanism of magneso-silicate composite.

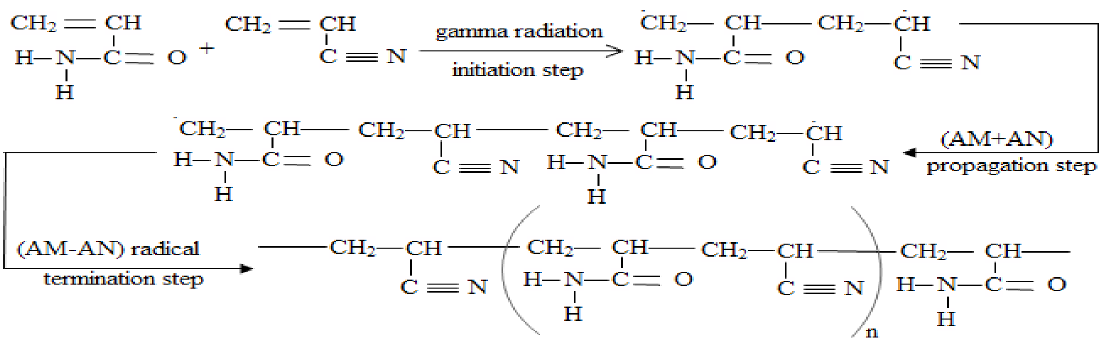
P(AM-AA), P(AM-AN), {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites were prepared as mentioned before in the experimental part by gamma radiation initiated co-polymerization of (AAM+AA), (AM+AN), (AM+AA+Mg+Si) and (AM+AN+Mg+Si) co-monomers at radiation doses 25, 65 and 90KGy. In gamma radiation initiated, the co-polymerization polymer complexes were formed which may be attributed to the possible steps**[19]:** preparation of the polymer by thegenerated radicals from the co-monomers, and the propagation of the co-monomer associated with the polymer by free radicals generated in the system**[16, 20]**.

The formationmechanism of P(AM-AA) copolymers can be represented as shown in scheme(2),when (AM+AA) co-monomer subjected to gamma radiation, breaking down was carried out for double bond of (AM) and (AA) to form covalent bond between C atoms of (AM) and (AA), the polymerization in the chain occurred by addition polymerization**[21]**. (AM+AA) free radical was obtained. (AM+AA) free radical react with (AM+AA) co-monomer to form chain propagation. Finally, the chains were coupled with another (AM-AA) free radicals to obtain P(AM-AA) copolymer.

The formation mechanism of P(AM-AN) copolymers can be shown in scheme (3), from this scheme;when(AM+AN) co-monomersubjected to gamma radiation, breaking down was carried out for double bond of (AM), (AN) to form covalent bond between C atoms of (AM) and (AN), the polymerization in the chain occurred by addition polymerization**[21]**.(AM+AN) free radical was obtained. (AM+AN) free radical react with (AM-AN) co-monomer to form chain propagation. Finally, the chains were coupled with another (AM-AN) free radicals to obtain P(AM-AN) copolymer.



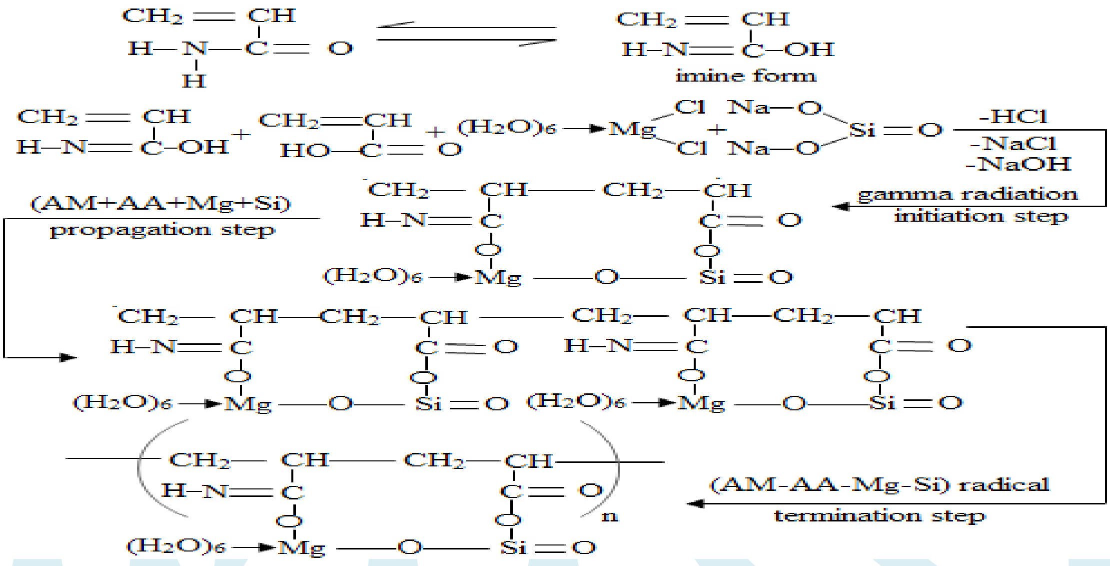
Scheme (2): Formation mechanism of polyacrylamide acrylic acid copolymer**.**



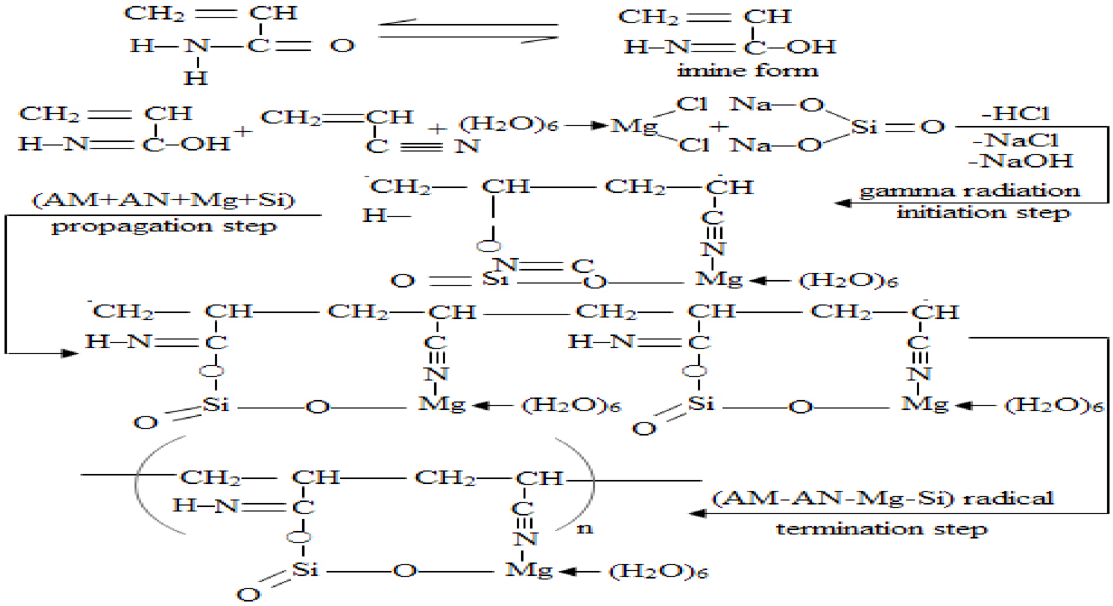
Scheme (3): Formation mechanism of polyacrylamide acrylonitrile copolymer.

The formationmechanism of {P(AM-AA)-MgSi} composite can be represented as shown in scheme (4),the reaction started by converting of (AM) monomer to imine form in solution. Then imine form react with (AA+Mg+Si) to form (AM-AA-Mg-Si) co-monomer, and subjected to gamma radiation, breaking down was carried out for double bond of (AM) and (AA) and formation of covalent bond between C atoms of (AM) and (AA), the polymerization in the chain between (AM) and (AA) occurred by addition polymerization, where polymerization of (Mg-Si) in the chain was occurred by condensation polymerization **[21]**by elimination of OH^- of carboxylate group of (AA) with Na^+ of Na_2SiO_3 to form ionic bond between O atom of carboxylate group and Si atom of Na_2SiO_3 and elimination of H^+ of imine form with $Cl^-$of $MgCl_2.6H_2O$ to form ionic bond between O atom of imine form and Mg atom of $MgCl_2.6H_2O$ and elimination Na^+ of Na_2SiO_3 with $Cl^-$of $MgCl_2.6H_2O$ to form ionic bond between O atom of Na_2SiO_3 and Mg atom of $MgCl_2.6H_2O$ to form (AM-AA-Mg-Si) free radicals. (AM-AA-Mg-Si) free radical react with (AM-AA-Mg-Si) co-monomer to form chain propagation. Finally, the chainswere coupled with another (AM-AA-Mg-Si) free radical to obtain {P(AM-AA)-MgSi} composite.

The formation mechanism of {P(AM-AN)-MgSi} composite was shown in scheme (5), the reaction started by converting of (AM) monomer to imine form in solution. Then imine form reacted with (AN+Mg+Si) to form (AM-AN-Mg-Si) co-monomer, and subjected to gamma radiation, breaking down carried out for double bond of (AM), and (AN), the polymerization in the chain between (AM) and (AN) occurred by addition polymerization, where polymerization of (Mg-Si) in the chain was occurred by condensation polymerization**[29]**, by elimination of $OH^-$of imine form with Na^+ of Na_2SiO_3 with formation of ionic bond between C atom of imine form and Si atom of Na_2SiO_3 and elimination Na^+ from Na_2SiO_3 with $Cl^-$of $MgCl_2.6H_2O$ with formation of ionic bond between O atom Na_2SiO_3 and Mg atom of $MgCl_2.6H_2O$ and elimination of H^+ of solution with $Cl^-$of $MgCl_2.6H_2O$ and lone pair of electron of N atom of (AN) were bonded by ionic bond with Mg atom of $MgCl_2.6H_2O$ to form (AM-AN-Mg-Si) free radical. (AM-AN-Mg-Si) free radical react with (AM-AN-Mg-Si) co-monomer to form chain propagation. Finally, the chains were coupled with another (AM-AN-Mg-Si) free radical to obtain {P(AM-AN)-MgSi} composite.



Scheme (4): Formation mechanism of polyacrylamide acrylic acid magnso-silicate composite



Scheme (5): Formation mechanism of polyacrylamide acrylonitrile magnso-silicate composite.

The prepared samples of P(AM-AA), P(AM-AN),{P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites are hard granulating in nature suitable for use in column operations with yellow color.

IR spectra of MgSiion exchanger was shown in Figure 1. (a), from this Figure six characteristic bands were observed in the regions 3150-3670, ~1652, 1000-1100, 903, 640 and ~470 cm^{-1}. The absorption band at 3150-3670cm^{-1} may be attributed to the stretching mode of water and OH groups absorbed on the compsite**[1,22,23]**. The strong band appear at ~1652 cm^{-1} represents the bending mode of water molecules absorbed on MgSicomposite **[1]**. The broad absorption band at 1000-1100cm^{-1} is due to the metal-oxygen (Mg-O) bond **[1]**.The band at ≈ 903 cm^{-1} may be due to the Mg-OH deformation vibration or overlapping of the Si-O and Si-OH, and Mg-O bonds in the structure **[1,24]**. The broad bands at 640 and 470 cm^{-1} are assigned to Si-O-Mg and Si-O-Si bending vibrations, respectively **[1,25]**.

IR spectra ofP(AM-AA) copolymers preparedat radiation doses 25, 65 and 90KGy was represented in Figure 2. (a), from this Figure two bands observed at 3450 and 3354cm^{-1}**[26].**The first band may be attributed to the stretching mode of N-H bond of acrylamide and the second band attributed to the stretching mode of O-H of acrylic acid **[27]**. The band appeared at 3210cm^{-1} cross ponding to the stretching mode of H-O-H bonded of water molecules **[28,29]**. The bands appeared at (3090, 2950 and 2870cm^{-1}) may be due to the stretching mode of C-H of acrylamide and acrylic acid **[30]**. The strong band appeared at 1720cm^{-1}attributed to the stretching mode ofcarbonyl group of acrylic acid **[22,31]**. Strong band appeared at 1550cm^{-1} attributed to the bending mode ofN-H bond of acrylamide**[32]**.Two bands appeared at 1450 and 1370cm^{-1}may be attributed to the bending mode of C-H of acrylamide and acrylic acid **[30,33]**. Two broad bands appeared at 1213 and 1022cm^{-1} attributed to the bending vibration of C-N of acrylamide **[33,34]**.

IR spectra ofP(AM-AN) copolymers preparedat radiation doses 25, 65 and 90KGy wasshown in Figure 2. (b),fromFigure represent,two bands appeared at 3340-3450 and 3195cm^{-1}may be attributed to the stretching vibration of N-H bond of acrylamide **[1,29]**. Two bands observed at 2935 and 2875cm^{-1} can be attributed to the stretching mode of C-H of acrylamide and acrylonitrile **[35,36].** The band appeared at 2790cm^{-1} may be due to the stretching mode of aldehyde group may be present by rearrangement in the structure **[31]**. The strong band appeared at 2244cm^{-1}due to the stretching mode of C≡N of acrylonitrile **[35-38].**The band appeared at 1665cm^{-1} attributed to the stretching mode ofcarbonylgroup of acrylamide **[32]**. Band appeared at 1605cm^{-1}may be attributed to the bending mode ofN-H bond of acrylamide**[32]**.Two bands observed at 1450 and 1409cm^{-1}may be attributed to the bending mode of C-H of acrylamide and acrylonitrile **[34-37]**. Three bands appeared at 1316, 1182 and 1120cm^{-1} attributed to the bending vibration of C-N of acrylamide and acrylonitrile **[32,34,37].**

IR spectra of{P(AM-AA)-MgSi} composites prepared at radiation doses 25, 65 and 90KGy was represented in Figure 2. (c), this Figure show that; broad band observed at 3460-3200cm^{-1} can be attributed to the stretching mode of water and OH group absorbed on the composites**[1]**. The two bands observed at 3460 and 3200cm^{-1} can be attributed to the stretching mode of N-H bond of acrylamide and H-O-H bonded of water molecules or O-H of acrylic acid respectively**[27]**. Two bands appeared at 2960 and 2875cm^{-1}may be due to the stretching mode of C-H of acrylamide and acrylic acid**[29-31]**. Weak band appeared at 2245cm^{-1}due to the stretching mode of C≡C bond may be present by rearrangement in the structure**[29,36]**. Two bands appeared at 1725 and 1675cm^{-1},the former band may be due to the stretching mode ofcarbonylgroup of acrylic acid **[26,32],** and the later band due to bending vibration of carbonylgroup of acrylamide or due to presence of imine group or O-H bonded water molecules absorbed on the composite **[32,39].**Band appeared at 1605cm^{-1} for {P(AM-AA)-MgSi}at radiation dose 90KGy attributed to the bending mode ofO-H bonded water molecules absorbed on the composite**[1]**. The band appeared at 1571cm^{-1}dueto the bending mode ofN-H bond of acrylamide**[32]**. Two bands appeared at 1451 and 1413cm^{-1}may be attributed to the bending mode of C-H of acrylamide and acrylic acid **[31,33,36]**.Two bands appeared at 1331 and 1218cm^{-1} for compositeat radiation doses 25 and 65KGy, where at 1331 and 1173cm^{-1}for compositeat radiation dose 90KGy may be attributed to the bending mode of C-N of acrylamide **[32]**.Band appeared at 1104cm^{-1}, this band reflect that metal oxygen bond Mg-O**[1,17,18]**. Three bands appeared at 793, 611 and 465cm^{-1}. The first band may be attributed to the of Mg-OH deformation vibration or overlapping of the Si-O and Si-OH and Mg-O bonds in the structure **[1,25]**. The second band may be attributed toSi-O-Mg bending vibrations **[25]**. The third band may be due to Si-O-Si bending vibrations **[1,25]**the bands at 1104, 793, 611 and 465 cm^{-1} indicated that impregnation of Mg and Si in the polymeric resin, these results were agree with data obtained from XRF as will be see later.

IR spectra of{P(AM-AN)-MgSi} composites prepared at radiation doses 25, 65 and 90KGy was shown in Figure 2. (d), from thisFigure broad band observed at 3475-3300cm^{-1} can be attributed to the stretching mode of water and OH group absorbed on the composite or N-H bond of acrylamide **[1,27]**.Two bands observedat 3190 and 2940cm^{-1} can be attributed to the stretching mode of N-H bond of acrylamide and C-H of acrylamide and acrylonitrile respectively,**[34,36]**.Strong band appeared at 2244cm^{-1}due to the stretching mode of C≡N bond of acrylonitrile **[36]**. Two bands appeared at 1661 and 1605cm^{-1}, the first band may be attributed to the bending mode C=O group of acrylamide or due to presence of imine group**[32]**, and the second band may be due to bending vibration of N-H bond of acrylamide or O-H bonded water molecules absorbed on the composite **[1,36]**.Two bands appeared at 1455 and 1413cm^{-1} attributed toC-Hof acrylamide and acrylonitrile **[30]**.Band appeared at 1571cm^{-1}may be attributed to the bending mode ofN-H bond of acrylamide**[32]**. Two bands appeared at 1451 and 1413cm^{-1}may be attributed to the bending mode of C-H of acrylamide and acrylic acid **[34-36]**.Two bands appeared at 1340 and 1220cm^{-1} for compositeat radiation dose 25KGy, where at 1340 and 1188cm^{-1}for compositeat radiation doses 65 and 90KGy may be attributed to the bending mode of C-N of acrylamide **[32]**.The band appeared at 1040cm^{-1} attributed to metal oxygen bond Mg-O**[1,17,18]**. Three bands appeared at 905, 636 and 460cm^{-1}). The first band may be attributed to the of Mg-OH deformation vibration or overlapping of the Si-O and Si-OH and Mg-O bonds in the structure **[1,25]**.The second band may be attributed toSi-O-Mg bending vibrations **[1,25]**.The third band may be due to Si-O-Si bending vibrations **[1,25]**.The bands at 1040, 905, 636 and 460cm^{-1} indicated that impregnation of Mg and Si in the structure of polymeric resin, these results were agree with data obtained from XRF as will be see later.

X-ray diffraction patterns of MgSi composite was represented in Figure 1. (b), from this Figure it is clear that MgSi has crystalline structure **[1,40]**. These results were agree with the data obtained from XRD of composites materials treated at different heating temperature **[1,11,14]**. The crystallinity of the prepared materials slightly improved with the increase of heating temperatures from 50^{o}C to 850±1^{o}C, and there is a sharp improvement of crystallinity occurs at 850±1°C.

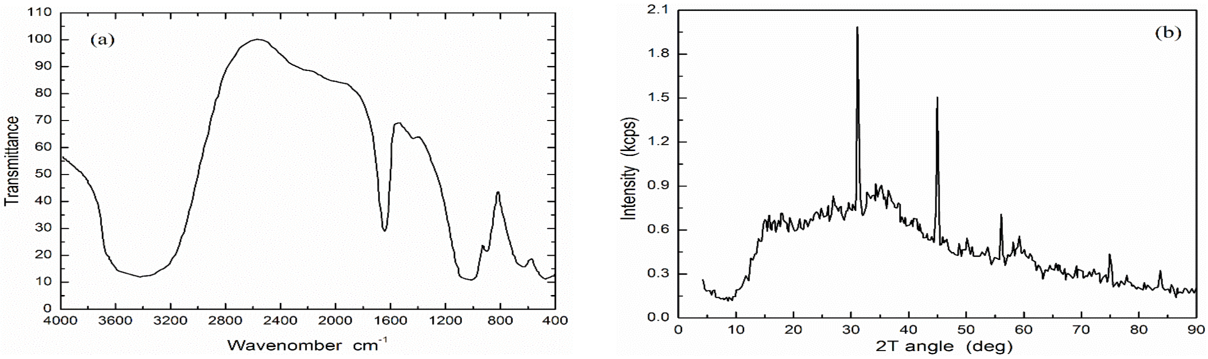


Figure 1. (a) IR spectrum of magneso-silicate; (b) XRD of magneso-silicate.

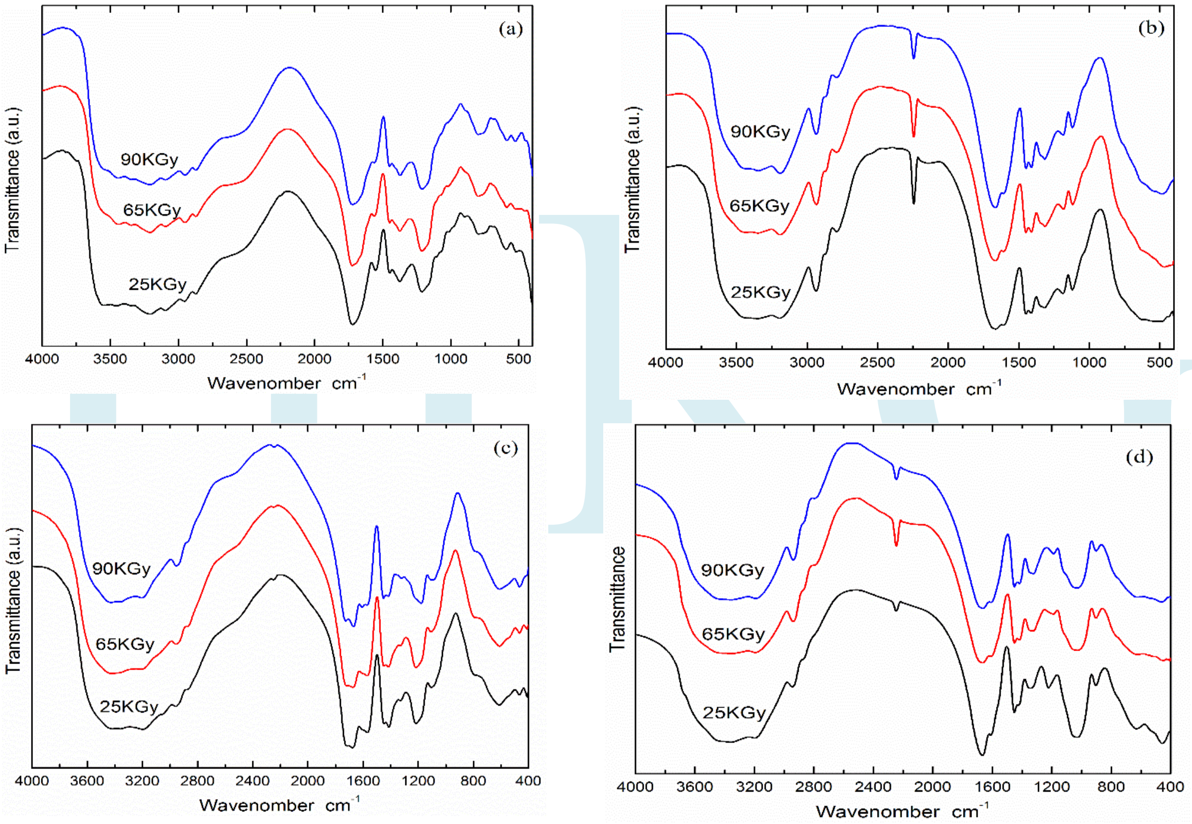


Figure 2. (a) IR spectrum of P(AM-AA); (b) P(AM-AN); (c) {P(AM-AA)-MgSi}; (d) {P(AM-AN)-MgSi} at different radiation doses.

Figure 3. (a), show that XRD of P(AM-AA) copolymers preparedat radiation doses 25, 65 and 90KGy. This Figureindicated that P(AM-AA) copolymers have amorphous structure and these results were similar to the data obtained from XRD of polyacrylamide-co-acrylic acid prepared by Hassan, et al. **[31]**. In addition, the crystalline character of the prepared samples was increased with radiation doses from 25 to 90KGy.Figure 3. (b) shows XRD patterns for P(AM-AN) copolymers preparedat radiation doses 25, 65 and 90KGy.From this figure it is clear that the sample prepared at radiation dose 25 KGy has crystalline structure, and these results were similar to the data obtained from XRD of

potassium hexacyano cobalt (II) ferrate (II) polyacrylonitrile (KCFC–PAN)**[41]**,where samples prepared at radiation doses 65 and 90KGy have amorphous structure.

Figure 3. (c and d) show XRD patterns of {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites prepared at radiation doses 25, 65 and 90KGy, respectively. From these figures it is clear that P(AM-AA)-MgSi and P(AM-AN)-MgSi have crystalline structure and these results were similar to the data obtained from XRD of polyacrylamide titanium tungstophosphate **[19,42]**, and potassium hexacyano cobalt (II) ferrate (II) polyacrylonitrile (KCFC–PAN)**[41].** In addition, the crystalline character of {P(AM-AA)-MgSi}samples were decreased with radiation dose from 25 to 90 KGy,where the samples prepared at radiation doses 25 and 65KGy have crystalline nature, where sample prepared radiation dose 90KGy have semi crystalline nature. On the other hand, the crystalline character {P(AM-AN)-MgSi} was decreased with radiation doses from 25 to 65KGy then increase from 65 to 90 KGy, where the sample at radiation dose 65 and 90 KGy has amorphous and semi crystalline natures, respectively.

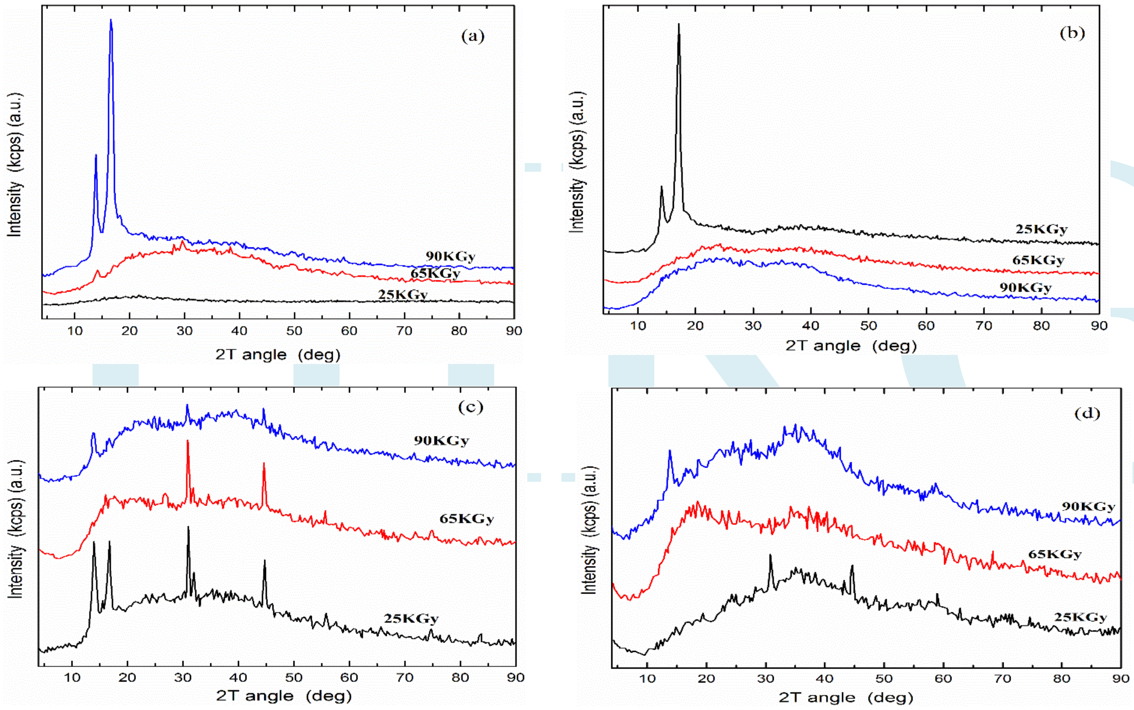


Figure 3. (a) XRD of P(AM-AA); (b) P(AM-AN); (c) {P(AM-AA)-MgSi}; (d) {P(AM-AN)-MgSi} at different radiation doses.

Differential thermal and thermogravimetric analyses (DTA&TGA) play a vital role in studying the structure and the properties of any materials where it has been widely used to investigate the decomposition characteristics of materials. DTA and TGA data were used here to provide an alternative model for the kinetics of the composite degradation. For all investigation studies of the composites the rate of heating is 10°C/min**[17,34,42,43],** and the data were tabulated in Tables 1 and 2. Table 1 was represented the data obtained for DTA and TGA analyses for inorganic ion exchange material MgSi and organic polymers P(AM-AA) and P(AM-AN) radiated at different radiation doses 25, 65 and 90 KGy. The data obtained are supporting the fact that MgSihave a good thermal stability comparing with the other inorganic ion exchangers and the weight loss of MgSiwhen the sample calcinated at 800 ^{0}C equal to 33.4%**[1].**

DTA and TGA of P(AM-AA) and P(AM-AN)copolymers prepared at radiation doses 25, 65 and 90KGy were represented in Table 1and indicates the process was occurring via five stage process and the weight loss are continued up to 500^{o}C. The weight loss for P(AM-AA)and P(AM-AN) prepared at radiation doses 25, 65 and 90KGy with the heating temperature indicates that a (67.15%, 100% and 68.3%) for P(AM-AA) and (56.98%, 61.3% and 25.5%) for P(AM-AN) when the samplesare calcinated at 500 ^{o}C**[19].**

The DTA and TGA analyses for polymeric materials impregnated with inorganic ion exchange materials, {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} prepared at different radiation doses 25, 65 and 90 KGy were measuredand tabulated in Table 2.The data in Table 2 indicates that the process for {P(AM-AA)-MgSi} composite was occurring via four stage process at radiation doses 25 and 90KGy, where five stage process at radiation doses 65KGy. On the other hand, the process for {P(AM-AN)-MgSi} prepared at radiation doses 25, 65 and 90 KGy was ocurrs via four stage process. Also, the datasupporting the fact that {P(AM-AA)-MgSi}composites prepared at radiation doses 25, 65 and 90KGy have a good thermal stability comparing with the other inorganic ion exchangers. The weight losses of {P(AM-AA)-MgSi}composites prepared at radiation doses 25, 65 and 90KGy with the heating temperature equal 100%, 88.34% and 88.8% when the samplesarecalcinated at 800 ^{0}C. also, Table 2 indices that, the weight loss for {P(AM-AN)-MgSi}prepared at radiation doses 25, 65 and 90KGy are continued up to 600^{o}C, and no weight loss occurred in the range ~600-800^{o}C.This supporting the fact that {P(AM-AN)-MgSi}prepared at radiation doses 25, 65 and 90KGy have a good thermal stability comparing with the other inorganic ion exchangers. The weight losses of {P(AM-AN)-MgSi}prepared at radiation doses 25, 65 and 90KGy with the heating temperature equal to 74.2%, 80.8% and 83.9% when the sample is calcinated at 800 ^{0}C**[1,19].**

The elemental analysesofmagneso-silicate and polymeric composites based on silicateprepared at different radiation doses were measured using XRF and tabulated in Table (3); the measured data is confirmed that impregnation of magneso-silicate in the{P(AM-AA)-MgSi} and{P(AM-AN)-MgSi}**[45].**

4- CONCLUSION

Magneso-silicate (MgSi) has been synthesized by precipitation technique. P(AM-AA), P(AM-AN), {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composites have been synthesized by subjected co-monomers to gamma radiation initiated polymerization at radiation doses 25, 65 and 90KGy. From the data obtained from the analytical techniques such as IR, XRD, TGA, DTA and XRF it is indicating that the impregnation of MgSi in {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} show an improvement in thermal stability and these composite materials have crystalline nature suitable for column chromatographic applications**[46].**

Table (1): DTA and TGA analyses for MgSi, P(AM-AA) and P(AM-AN) materials.

Composite	Radiation Dose, KGy	Temp., °C	Temp. Range, °C	Peak	Peak Description	Ref.	Water Loss	% Total water loss
MgSi	-	128.35	43-192	Endo.	Crossbedding loss of free water	1,47	16.2	33.7
	-	257.2	192-283	Exo.	Due to decomposition of residual OH-groups and condensation of non-bonded oxygen	48	4.45	
	-	501.16	283-800	Endo.	The loss of chemical bond water	1,47	12.79	
P(AM-AA)	25	69.29	44-125	Endo.	Loss of external water molecule	49	5.95	50.2
		219.88	125-240	Endo.	Removal of the water of crystallization for P(AM-AA)	50	8.94	
		338.27	240-384	Endo.	Probably caused by the dehydration of carboxylic acid and decarboxylation or the loss of chemical bond water	1,47,51	28.1	
		400.9	384-408	Exo.	May be due to the complete decomposition of the organic part of the materials	52-54	9.87	
		422.28	408-500	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	14.02	
	65	86.6	40-137	Endo.	Loss of external water molecule	49	8.6	100
		219	137-253	Endo.	Removal of the water of crystallization for P(AM-AA)	50	22.06	
		330.7	253-352	Endo.	Probably caused by the dehydration of carboxylic acid and decarboxylation or the loss of chemical bond water	1,47,51	28.3	
		362.47	352-378	Exo.	may be due to the complete decomposition of the organic part of the materials	52-54	25.64	
		392.56	378-500	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	51.76	
	90	81.69	41-129	Endo.	Loss of external water in the resin	49	4.08	68.5
		222.45	129-248	Endo.	Removal of the water of crystallization for P(AM-AA)	50	9.79	
		274.7	248-311	Exo.	Since the complete decomposition of the organic part of the materials	52-54	6.72	
		320.9	311-347	Endo.	Due to dehydration of carboxylic acid and decarboxylation or the loss of chemical bond water	1,47,51	7.64	
		350.08	347-367	Exo.	the complete decomposition of the organic part of the materials	52-54	5.5	
		386.55	367-398	Endo.	The loss of constitution water, which forms part of the crystalline network and it is generally presented like OHgroups	55-56	17.9	
		420.34	398-427	Exo.	may be due to the complete decomposition of the organic part of the composites	52-54	8.8	
		476.5	427-500	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	7.87	
P(AM-AN)	25	80.5	54-133	Endo.	loss of external water present in the composite	49	8.21	57.07
		273.15	133-328	Endo.	Due to removal of the water of crystallization for P(AM-AN) copolymer	50	16.46	
		372.48	328-384	Exo.	Due to the complete decomposition of the organic part of the materials	52-54	12.5	
		393.57	384-418	Endo.	The loss of constitution water, which forms part of the crystalline network and it is generally presented like OH groups	55,56	12.3	
		436.44	418-452	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid	51	5.34	
		465.7	452-500	Endo.			2.05	
	65	83.43	50-145	Endo.	Lossof external water molecule	49	9.5	61.39
		273.39	178-312	Endo.	Removal of the water of crystallization for P(AM-AN)	50	14.3	
		362.8	312-367	Exo.	Due to the complete decomposition of the organic part of the polymer	52-54	8.27	
		378.22	367-400	Endo.	The loss of constitution water, which forms part of the crystalline network and it is generally presented like OH groups	55,56	14.28	
		469.76	400-500	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	14.68	
	90	85.63	57-137	Endo.	loss of external water molecule	49	4.78	25.5
		240.47	137-286	Endo.	removal of the water of crystallization for P(AM-AN)	50	6.04	

		357.41	286-416	Endo.	The loss of constitution water, which forms part of the crystalline network and it is generally presented such asOH groups	55,56	10.09	
		437.84	416-456	Exo.	Dueto the complete decomposition of the organic part of the resin	52-54	2.29	
		469.5	456-500	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	2.11	

Table (2): DTA and TGA analyses for {P(AM-AA)-MgSi} and {P(AM-AN)-MgSi} composite materials.

Composite	Radiation Dose, KGy	Temp., °C	Temp. Range, °C	Peak	Peak Description	Ref.	Water Loss	% Total water loss
P(AM-AA)-MgSi	25	80.92	38-139	Endo.	Caused by loss of external water molecule	49	9.33	100
		263.72	139-313	Endo.	Removal of the crystalline water for {P(AM-AA)-MgSi}	50	14.66	
		396.14	340-434	Exo.	Thecomplete decomposition of the organic part of the composite.	52-54	1858	
		434.18	434-517	Endo.	Probably caused by the dehydration of carboxylic acid and decarboxylation or the loss of chemical bond water	1,47,49,51	17.71	
		655.6	517-800	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	40.9	
	65	92.17	67-164	Endo.	Loss of external water molecule	49	6.48	88.34
		304.5	164-355	Endo.	Removal of the chemical bond water of {P(AM-AA)-MgSi}	50	22.45	
		375.15	355-409	Exo.	Thecomplete decomposition of the organic part of the composite resin	52-54	12.18	
		429.19	409-455	Exo.			7.01	
		521.19	455-563	Exo.			37.38	
	90	80.8	42-171	Endo.	Loss of free water molecule	49	6.6	88.8
		240.16	171-318	Endo.	Removal of the crystalline water for {P(AM-AA)-MgSi}	50	14.32	
		380.33	318-407	Exo.	The complete decomposition of the organic part of the composite ion exchangers	52-54	19.85	
		420.55	407-431	Endo.	Due to loss of chemical bond water	1,47	3.35	
		444.05	431-467	Exo.	Maybe due to the complete decomposition of the organic part of the materials	52-54	5.88	
		503.78	467-800	Exo.			38.64	
P(AM-AN)-MgSi	25	76.26	57-132	Endo.	Loss of water molecule	49	8.77	74.2
		281.69	132-340	Endo.	Removal of the water of crystallization for {P(AM-AN)-MgSi}	50	13.11	
		372.13	340-398	Exo.	The complete decomposition of the organic part of the composites	52-54	9.97	
		419.69	398-433	Endo.	The loss of interstitial water molecules	1,47	4.78	
		515.58	434-577	Exo.	May be due to the complete decomposition of the organic part of the materials	52-54	32.49	
		585.56	577-800	Endo.	The chain scission in the main chain of poly acrylamide acrylic acid.	51	4.45	
	65	76.24	40-124	Endo.	Loss of free water molecule	49	8.85	80.8
		263.51	124-334	Endo.	Removal of the water bind moleculesof {P(AM-AN)-MgSi}	50	14.33	
		362.72	334-383	Exo.	Thecomplete decomposition of the organic part of the ion exchange materials	52-54	8.31	
		398.57	383-402	Endo.	The loss of chemical bond water	1,47	2.86	
		448.38	402-472	Exo.	May be due to the complete decomposition of the organic part of the materials	52-54	8.87	
		521.29	472-800	Exo.			37.44	
	90	76.11	55-126	Endo.	Loss of non-bonded water molecule	49	7.29	83.9
		272.63	126-326	Endo.	Removal of the water of crystallization for {P(AM-AN)-MgSi}	50	14.3	
		365.2	326-397	Exo.	may be due to the complete decomposition of the organic part of the materials	52-54	12.73	

		421.29	397-452	Endo.	The loss of chemical bond water	1,47	7.88	
		527.2	452-800	Exo.	Thecomplete decomposition of the organic part of the composite materials	52-54	41.2	

Table (3): Elemental analysis of magneso-silicate and polymeric composites based on silicate prepared at different radiation doses

Composite	**Radiation Dose, KGy**	**Concentration, %**	
		Mg	**Si**
MgSi	----	18.7	37.7
P(AM-AA)-MgSi	25	10.1	21.2
	65	11.6	25.6
	90	8.3	44.7
P(AM-AN)-MgSi	25	13.3	44.7
	65	12.9	47.6
	90	13.5	45.2

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